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Issued November 2, 1907.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN No. 49.
MILTON WHITNEY, Chief.

THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL CARBONATES.

BY

FRANK K. CAMERON AND JAMES M. BELL.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.

1907.

LETTER OF TRANSMITTAL.

UNITED STATES DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS,
Washington, D. C., July 20, 1907.

SIR: I transmit herewith a technical paper by Frank K. Cameron and James M. Bell, entitled *The Action of Water and Aqueous Solutions upon Soil Carbonates*, which I recommend to be published as Bulletin No. 49 of this Bureau. The manuscript has been gone over with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its publication.

Very respectfully,

MILTON WHITNEY,
Chief of Bureau.

HON. JAMES WILSON,
Secretary of Agriculture.

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THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL CARBONATES.

INTRODUCTION.

Lime as a mineral constituent of soil amendments or fertilizers has always occupied a prominent place in soil chemistry. It is usually applied to the soil as a sulphate (gypsum or land plaster), phosphate, hydrate (or oxide), or carbonate. The solubility of these substances is obviously of the utmost importance in determining their distribution and effectiveness when applied to the soil. Nevertheless, the literature regarding their solubilities has been most confusing and contradictory, and in consequence agricultural investigations have suffered seriously in that observations have been interpreted in the light of uncertain or conflicting premises. In many cases, indubitably, the truth has been missed on this account and conclusions deduced which have not only delayed or misguided scientific investigation, but have led to serious disappointment when brought under the test of actual farm practice. For these reasons the investigation of the fundamental solubility data and the chemical relations between the lime salts and aqueous solutions has been deemed necessary in the studies which this Bureau is prosecuting on soils and fertilizers.

The present state of our knowledge as regards the solubility of the sulphate^a and the phosphates^b of calcium has been shown in recent publications of the Bureau. The present bulletin contains similar data for the hydrates and carbonates of lime; and since magnesia and its compounds are so closely related to lime and its corresponding compounds, both in chemical properties and mineral associations, data for the hydrates and carbonates of magnesia are also included. In searching the literature for the material contained in this bulletin an enormous number of papers was found, especially with regard to the solubility of lime carbonates. Many of these, however, it has not been deemed wise to cite—when they had only a local or fugitive interest, when they were of a qualitative nature only, when they would add but further and unnecessary confirmation

^a Bul. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906).

^b Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. (1907).

to points brought out by other data cited, or when, as occasionally happened, they were obviously trivial or of doubtful accuracy. It is believed, however, that the data given will furnish an approximately complete statement of our present knowledge of the subject. It is also believed that this material will have an interest for geologists and certain technical manufacturers second only to that for agriculturists.

One of the great agricultural problems of the United States is the alkali, or accumulation of soluble salts frequently found in the soils of the arid areas of some of the Western States, and to a proper understanding and satisfactory handling of this important practical problem, a knowledge of the chemistry of the solutions formed by the action of water on the mineral components of these soils is of fundamental importance. The chemistry of "white alkali" has been treated quite fully in previous publications of this Bureau and especially the important reactions between gypsum and solutions of the more soluble salts found in the soil. The present bulletin brings together our knowledge of the reactions between the same solutions and calcium carbonate, the immediate source of the much-dreaded "black alkali." An intelligent interpretation can now be made of the analyses of drainage waters and the changes in the soil which they indicate. A scientific foundation is now prepared for the further development of practical methods for handling this important agricultural problem.

CARBON DIOXIDE.

SOLUBILITY OF CARBON DIOXIDE IN WATER.

The solubility in water of carbon dioxide, like all other gases, is greater at the lower temperatures than at the higher temperatures. With one or possibly two known exceptions, the solubility in aqueous solutions is decreased by increasing quantities of the material in solution. Thus, the solubility of carbon dioxide in water is decreased either by increasing the temperature or by the addition of some material, such as sodium chloride or other salts. The results of the work recorded in the literature have been assembled and are given in the following tables. The results are given in the same form as they have been recorded in the original papers. For instance, the solubility of carbon dioxide in water at 10° C. has been given by Bunsen as 1.1847. This means that one cubic centimeter of water at 10° will dissolve the quantity of carbon dioxide occupying 1.1847 cubic centimeters at 0° and 760 mm. *All the gaseous volumes are reduced to 0° and 760 mm. pressure.* In this way comparisons may be made between the solubility of the gas in solvents at different temperatures and also in different solutions.

TABLE I.—*Solubility of carbon dioxide in water at different temperatures.*

Temperature.	Bunsen. ^a	Setschenow. ^b	v. Wroblewski. ^c	Bellati and Lusana. ^d	Bohr and Beck. ^e	Prytz and Holst. ^f	Bohr. ^g	Geffcken. ^h
° C.								
0	1.7967	1.797	1.7308	1.713
1	1.7207	1.646
2	1.6481	1.548
3	1.5787	1.527
4	1.5126	1.473
5	1.4497	1.424
6	1.3901	1.377
7	1.3339	1.331
8	1.2809	1.282
9	1.2311	1.237
10	1.1847	1.194
10.75	1.1281
11	1.1416	1.154
12	1.1018	1.117
12.43	1.086
12.68	1.0414
13	1.0653	1.083
14	1.0321	1.050
15	1.0020	1.019	1.070
15.2	1.0090
16	.9753985
17	.9519956
17.19619
17.6932
18	.9318928
18.38896
19	.9150902
19.3885
20	.9014878
21838854
21.7825
22829
22.178375
22.4	.8642
23798804
24781
25759	.8255
26738
27718
28699
29682
30665
35592
37.29	0.5629
40530
45479
50436
55394
60359
1002438

^a Ann. Chem. Pharm., **93**, 1 (1855); Phil. Mag. (4), **9**, 116, 181 (1855).^b Arch. gesamt. Physiol., **8**, 1 (1874); Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886); **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).^c Ann. Phys. Chem., **254**, 290 (1883).^d Atti Ist. Veneto (6), **7** (1889); abstr. in Beibl. Ann. Phys. Chem., **14**, 18 (1890).^e Ann. Phys. Chem., **280**, 318 (1891).^f Ann. Phys. Chem., **290**, 130 (1895).^g Ann. Phys. Chem., **304**, 500 (1899).^h Zeit. phys. Chem., **49**, 257 (1904).TABLE II.—*Solubility of carbon dioxide in water under different pressures.^a*

Pressure.	Solubility at—	
	0° C.	12.43° C.
<i>Atmospheres.</i>		
1	1.797	1.086
5	8.65	5.15
10	16.03	9.65
15	21.95	13.63
20	26.65	17.11
25	30.55	20.31
30	33.74	23.25

^a v. Wroblewski, Ann. Phys. Chem., **254**, 290 (1883).

It will be seen that at the higher pressures the solubility of carbon dioxide in water is not proportional to the pressure as would be expected from Henry's law. At the lower pressures, below 5 atmospheres, the solubility is almost proportional to the pressure.

SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS.

Sulphuric acid.

TABLE III.—*Solubility of carbon dioxide in aqueous solutions of sulphuric acid.*^a

H ₂ SO ₄ per liter.	Solubility at—	
	15° C.	25° C.
<i>Grams.</i>		
25.1	1.016	0.7923
25.3	1.016	.7936
47.8	.9772	.7693
50.9	.9775	.7685
52.3	.9756	.7672
95.8	.9175	.7302
102.3	.9143	.7273
185.7	.8354	.6736
186.2	.8385	.6747

^a Geffcken, Zeit. phys. Chem., **49**, 257 (1904).

TABLE IV.—*Solubility of carbon dioxide in various mixtures of sulphuric acid and water at 17° C.*^a

H ₂ SO ₄ in solution.	Solubility.	H ₂ SO ₄ in solution.	Solubility.
<i>Per cent.</i>		<i>Per cent.</i>	
100.0	0.932	84.5	0.660
96.8	.852	73.1	.705
92.0	.719	8.58	.857

^a Satschenow, Mélanges phys. et chim. du bul. de l'acad. impér. des sci. de St.-Petersb., **9**, 617 (1876), Ann. Chim. Phys. (6), **25**, 226 (1892).

Tables III and IV show that in the comparatively weak solutions of sulphuric acid the solubility of carbon dioxide is decreased by increasing that concentration. On the other hand, starting from sulphuric acid (100 per cent H₂SO₄) the solubility of carbon dioxide is decreased by the addition of water, in which the solubility of the gas is less than in either sulphuric acid or pure water.

Nitric acid.

TABLE V.—*Solubility of carbon dioxide in aqueous solutions of nitric acid.*^a

HNO ₃ per liter.	Solubility at—	
	15° C.	25° C.
<i>Grams.</i>		
29.7	1.073	0.8382
29.9	1.075	.8366
35.1	1.069	.8387
44.4	1.080	.8447
87.1	1.093	.8620
87.4	1.093	.8622
117.2	1.105	.8752
158.7	1.109	.8839
160.0	1.111	.8865

^a Geffcken, Zeit. phys. Chem., **49**, 257 (1904).

Nitric acid solutions form the striking exception to the generality that the solubility of carbon dioxide is decreased by the addition of some other solute. It will be seen from Table V that the solubility of carbon dioxide is increased by adding nitric acid to the solution.

Hydrochloric acid.

TABLE VI.—*Solubility of carbon dioxide in aqueous solutions of hydrochloric acid, a*

HCl per liter.	Solubility at—	
	15° C.	25° C.
<i>Grams.</i>		
18.2	1.041	0.8047
18.7	1.042	.8074
44.2	1.020	.7973
45.6	1.023	.7984
75.9	0.9864	.7951
79.6	1.009	.7951

^a Geffcken. Zeit. phys. Chem., 49, 257 (1904).

Citric acid.

TABLE VII.—*Solubility of carbon dioxide in aqueous solutions of citric acid at 15.2°.*^a

Citric acid per liter.	Solubility.	Citric acid per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
12	1.007	198	0.893
49	.975	298	.841
99	.950	595	.719

^a Setschenow, Ann. Chim. Phys. (6), 25, 226 (1892).

Sodium chloride.

TABLE VIII.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride at different temperatures.*

Temper- ature.	6.52 ^a per cent solution.	7.062 ^b per cent solution.	12.995 ^b per cent solution.	17.42 ^b per cent solution.	17.62 ^a per cent solution.	26.00 ^b per cent solution.	5 ^c per cent solution.
° C.							
0	1.234				0.678		
5	1.024				.577		
6.4		0.8990	0.6326	0.5181		0.3470	
10	.875				.503		
15	.755	.7347	.5569	.4306	.442	.2969	0.8122
20	.664				.393		
22			.4822	.3892		.2630	
25	.583				.352		
30	.517				.319		
35	.460				.288		
40	.414				.263		
45	.370				.235		
50	.335				.215		
55	.305				.198		
60					.183		

^a Bohr, Ann. Phys. Chem., 304, 500 (1899).

^b Mackenzie, Ann. Phys. Chem., 237, 438 (1877).

^c Ssetschenow, Arch. gesamt. Physiol., 8, 1 (1874).

TABLE IX.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride.*^a

NaCl per liter.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
<i>Grams.</i>			
32	0.866	0.795	0.726
64	.760	.702	.630
96	.661	.610	.560
128	.580	.533	.497
160	.515	.483	.437
192	.466	.427	.394

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 226 (1892).

TABLE X.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride at 15.2° C.*^a

NaCl per liter.	Solubility.	NaCl per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
12.9	0.978	78.9	0.728
18.6	.950	105.2	.640
19.7	.944	125.6	.606
25.9	.919	157.8	.530
38.8	.865	210.4	.422
52.6	.802	315.6	.290
63.1	.778		

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), **34**, No. 3 (1886); Ann. Chim. Phys. (6), **25**, 226 (1892).

In Table XI there have been collected several isolated determinations by Setschenow, which are given for the sake of completeness.

TABLE XI.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride.*^a

Composition of solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
125.6 grams NaCl per liter (A)	0.606	0.550
100 c. c. solution A + 95.6 grams water776	.705
100 c. c. solution A + 296.8 grams water885	.807
11.7 per cent solution			0.489
19.7 per cent solution341

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

Potassium chloride.

TABLE XII.—*Solubility of carbon dioxide in aqueous solutions of potassium chloride at different temperatures.*^a

Density of solution.	KCl in solution.	Solubility at—		
		8° C.	15° C.	22° C.
	<i>Per cent.</i>			
1.0211	6.06	0.9880	0.7772	0.6701
1.0527	8.65	.9178	.7768	.6488
1.0796	11.97	.8639	.7202	.5970
1.1488	22.51	.6877	.5707	.4801

^a Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

TABLE XIII.—*Solubility of carbon dioxide in aqueous solutions of potassium chloride.*

Setschenow. ^a		Geffcken. ^b		
KCl per liter.	Solubility at 15.2° C.	KCl per liter.	Solubility at—	
			15° C.	25° C.
<i>Grams.</i>		<i>Grams.</i>		
94	0.819	31.55	0.9892	0.7695
141	.745	32.23	.9865	.7667
282	.579	77.96	.8875	.6920
-----		78.93	.8910	.691

^a Ann. Chim. Phys. (6), **25**, 226 (1892).^b Zeit. phys. Chem., **49**, 257 (1904).

One other determination has been made by Setschenow,^a viz, that at 22.4° C. the solubility of carbon dioxide in 14.9 per cent potassium chloride solution is 0.589.

Ammonium chloride.TABLE XIV.—*Solubility of carbon dioxide in aqueous solutions of ammonium chloride at different temperatures.^a*

Density of solution.	NH ₄ Cl in solution.	Solubility at—		
		10° C.	15° C.	22° C.
	<i>Per cent.</i>			
1.0211	6.47	1.0227	0.8253	0.7182
1.0470	8.72	1.0000	.7906	.7022
1.0527	12.73	.9220	.7981	.6840
1.0721	22.23	.8132	.7384	.5998

^a Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).TABLE XV.—*Solubility of carbon dioxide in aqueous solutions of ammonium chloride at 15.2° C.^a*

NH ₄ Cl per liter.	Solubility.	NH ₄ Cl per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
1.0	1.005	86	0.897
10.0	.985	129	.858
43.0	.956	172	.819
51.6	.941	258	.770
64.5	.931	-----	

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

In the first of the above papers Setschenow has recorded that at 21.7° C. the solubility of carbon dioxide in 17.8 per cent of ammonium chloride solution is 0.669.

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Cæsium and rubidium chlorides.

TABLE XVI.—*Solubility of carbon dioxide in aqueous solutions of the chlorides of cæsium and rubidium.*^a

Solution.	Solubility at—	
	15° C.	25° C.
93.1 grams CsCl per liter.....	1.000	0.777
58.1 grams RbCl per liter.....	.991	.770
122.2 grams RbCl per liter.....	.921	.717

^a Geffcken, Zeit. phys. Chem., **49**, 257 (1904).

Lithium chloride.

TABLE XVII.—*Solubility of carbon dioxide in aqueous solutions of lithium chloride at 15.2° C.*^a

LiCl per liter.	Solubility.	LiCl per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
16.72	1.035	125.4	0.596
25.08	.899	250.8	.497
50.15	.808	501.5	.120

^a Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

Sodium bromide.

TABLE XVIII.—*Solubility of carbon dioxide in aqueous solutions of sodium bromide at 15.2° C.*^a

NaBr per liter.	Solubility.
115.1	0.775
460.3	.364
690.4	.221

^a Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

Potassium bromide.

TABLE XIX.—*Solubility of carbon dioxide in aqueous solutions of potassium bromide.*

Setschenow. ^a		Geffcken. ^b		
KBr per liter.	Solubility at 15.2° C.	KBr per liter.	Solubility at—	
			15° C.	25° C.
<i>Grams.</i>		<i>Grams.</i>		
83.9	0.908	65.51	0.9783	0.7621
167.7	.819	67.30	.9766	.7619
251.5	.748	125.8	.9100	.7030
503.1	.579	126.7	.9065	.7068

^a Ann. Chim. Phys. (6), **25**, 226 (1892).^b Zeit. phys. Chem., **49**, 257 (1904).

Potassium iodide.

TABLE XX.—*Solubility of carbon dioxide in aqueous solutions of potassium iodide.*

Setschenow. ^a		Geffcken. ^b		
KI per liter.	Solubility at 15.2° C.	KI per liter.	Solubility at—	
			15° C.	25° C.
<i>Grams.</i>		<i>Grams.</i>		
319.1	0.773	93.85	0.9809	0.7678
478.6	.688	95.18	.9835	.7676
957.3	.506	173.24	.9144	.7236
		185.87	.9090	.7166

^a Ann. Chim. Phys. (6), **25**, 226 (1892).^b Zeit. phys. Chem., **49**, 257 (1904).

Sodium nitrate.

TABLE XXI.—*Solubility of carbon dioxide in aqueous solutions of sodium nitrate at 15.2° C.^a*

NaNO ₃ per liter.	Solubility.	NaNO ₃ per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
89.3	0.835	208.4	0.621
104.2	.795	312.6	.495
125.0	.762	416.8	.385
156.3	.709	625.2	.244

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **34**, No. 3 (1886); Ann. Chim. Phys. (6), **25**, 226 (1892).TABLE XXII.—*Solubility of carbon dioxide in aqueous solutions of sodium nitrate at various temperatures.^a*

Solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
17.02 per cent solution.....		0.822	0.551
28.36 per cent solution.....			.400
125.4 grams per liter (A).....	0.747	.693	
100 c. c. (A) + 95.54 c. c. water.....	.876	.798	
100 c. c. (A) + 286.6 c. c. water.....	.946	.870	

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

Potassium nitrate.

TABLE XXIII.—*Solubility of carbon dioxide in aqueous solutions of potassium nitrate.*

Setschenow. ^a		Geffcken. ^b		
KNO ₃ per liter.	Solubility at 15.2° C.	KNO ₃ per liter.	Solubility at	
			15° C.	25° C.
<i>Grams.</i>		<i>Grams.</i>		
58.8	0.959	54.24	1.001	0.7825
117.5	.8902	104.0	.943	.745
168.0	.825			
235.1	.781			

^a Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **35**, No. 7 (1887).^b Zeit. phys. Chem., **49**, 257 (1904).

In the first of the above papers Setschenow gives the solubility of carbon dioxide in 20.24 per cent solution of potassium nitrate as 0.641 at 22.4° C.

Ammonium nitrate.

TABLE XXIV.—*Solubility of carbon dioxide in aqueous solutions of ammonium nitrate at 15.2° C.^a*

NH ₄ NO ₃ per liter.	Solubility.	NH ₄ NO ₃ per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
2.8	1.013	101.0	0.962
5.6	1.010	202.1	.911
11.2	1.006	386.0	.819
22.5	.983	404.3	.807
55.0	.989	810.4	.612

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 226 (1892).

Ammonium sulphate.

The following figures give two determinations of Setschenow* on the solubility of carbon dioxide in ammonium sulphate solutions:

Grams (NH ₄) ₂ SO ₄ per liter.....	72.2	144.4
Solubility at 15.2° C.....	0.712	0.575

Sodium sulphate.

TABLE XXV.—*Solubility of carbon dioxide in aqueous solutions of sodium sulphate at 15.2° C.^a*

Na ₂ SO ₄ per liter.	Solubility.	Na ₂ SO ₄ per liter.	Solubility.
<i>Grams.</i>		<i>Grams.</i>	
14.22	0.950	94.8	0.620
28.44	.876	142.2	.485
56.88	.753	284.4	.2335
71.10	.700

^a Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

TABLE XXVI.—*Solubility of carbon dioxide in aqueous solutions of sodium sulphate at various temperatures.^a*

Solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
7.11 per cent solution.....		0.670	
14.22 per cent solution.....			0.391
128.74 grams per liter (A).....	0.472	.470	
100 c. c. (A) + 98.04 c. c. water.....	.771	.660	
100 c. c. (A) + 294.12 c. c. water.....	.850	.771	

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

* Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Potassium sulphocyanate.TABLE XXVII.—*Solubility of carbon dioxide in aqueous solutions of potassium sulphocyanate at 15.2° C.^a*

KSCN per liter.	Solubility.
<i>Grams.</i>	
326	0.691
489	.590
978	.387

^a Setschenow, Ann. Chim. Phys. (6), 25, 229 (1892).**Sodium chlorate.**TABLE XXVIII.—*Solubility of carbon dioxide in aqueous solutions of sodium chlorate at 15.2° C.^a*

NaClO ₃ per liter.	Solubility.
<i>Grams.</i>	
233.3	0.625
349.9	.506
699.8	.257

^a Setschenow, Ann. Chim. Phys. (6), 25, 229 (1892).**Calcium chloride.**TABLE XXIX.—*Solubility of carbon dioxide in aqueous solutions of calcium chloride at various temperatures.^a*

Density.	CaCl ₂ in solution.	Solubility at—			
		8° C.	16½° C.	22° C.	30° C.
	<i>Per cent.</i>				
1.0358	4.3650	0.9423	0.7587	0.6726	0.5957
1.0489	5.7390	.8548	.7260	.6159	.5266
1.0683	8.0453	.8383	.6740	.5809	.4998
1.1387	15.7925	.6315	.5202	.4709	.3945

^a Mackenzie, Ann. Phys. Chem., 237, 438 (1877).**Strontium chloride.**TABLE XXX.—*Solubility of carbon dioxide in aqueous solutions of strontium chloride at various temperatures.^a*

Density.	SrCl ₂ in solution.	Solubility at—			
		8° C.	16½° C.	22° C.	30° C.
	<i>Per cent.</i>				
1.0873	9.5108	0.7789	0.6633	0.5806	0.5079
1.1159	12.3248	.7367	.5859	.5071	.4386
1.1727	17.7132	.6057	.4727	.4435	.3672
1.3428	31.1937	.2854	.2449	.2474	.2231

^a Mackenzie, Ann. Phys. Chem., 237, 438 (1877).

Another determination by Setchenow* is that at 15.2° C. the solubility of carbon dioxide in 3.97 per cent strontium chloride solution is 0.893.

Barium chloride.

TABLE XXXI.—*Solubility of carbon dioxide in aqueous solutions of barium chloride at various temperatures.*^a

Density.	BaCl ₂ in solution.	Solubility at—			
		8° C.	16½° C.	22° C.	30° C.
	<i>Per cent.</i>				
1.0684	7.3162	0.9694	0.7441	0.6803	0.5655
1.0916	9.7531	1.0207	.6445	.6072	.5426
1.1372	14.0297	-----	.6179	.5235	.4672
1.2731	25.2146	.4949	.6179	.3833	.3152

^a Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

Two determinations have been made by Setchenow,* as follows:

At 15.2° C. solubility in 5.2 per cent BaCl₂ solution is 0.894.

At 22° C. solubility in 6.94 per cent BaCl₂ solution is 0.670.

Magnesium sulphate.

TABLE XXXII.—*Solubility of carbon dioxide in aqueous solutions of magnesium sulphate at 15° to 16° C.*

MgSO ₄ per liter.	Solubility.
<i>Grams.</i>	
26.5	0.901
40.0	.822
79.5	.669
159.0	.441
318.0	.188

^a Setchenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

In Table XXXII the concentrations have been calculated from tables of the solubility of magnesium sulphate in water, as the original paper gave only the density of the concentrated solution, which was also saturated.

TABLE XXXIII.—*Solubility of carbon dioxide in aqueous solutions of magnesium sulphate at various temperatures.*^a

Composition of solution.	Temperature.	Solubility.
	°C.	
8.432 grams MgSO ₄ +500 grams water.....	26.00	0.712
33.73 grams MgSO ₄ +500 grams water.....	25.00	.586
60.2 grams MgSO ₄ +500 grams water.....	18.38	.523
15.05 per cent solution.....	22.40	.310

^a Setchenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 225 (1892).

*Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Zinc sulphate.TABLE XXXIV.—*Solubility of carbon dioxide in aqueous solutions of zinc sulphate at 15° to 16° C.^a*

ZnSO ₄ per liter.	Solubility.
<i>Grams.</i>	
38.3	0.903
76.7	.783
230.0	.474
460.0	.209

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), 35, No. 7 (1887); Ann. Chim. Phys. (6), 25, 226 (1892).

In Table XXXIV the concentrations have been calculated from tables of the solubility of zinc sulphate in water, as the original papers gave only the density of the most concentrated solution, which was also saturated.

TABLE XXXV.—*Solubility of carbon dioxide in aqueous solutions of zinc sulphate at various temperatures.^a*

Composition of solution.	Temperature.	Solubility.
	° C.	
9.84 grams ZnSO ₄ +500 grams water.....	26.00	0.715
39.34 grams ZnSO ₄ +500 grams water.....	25.00	.593
80.7 grams ZnSO ₄ +500 grams water.....	18.38	.522

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), 22, No. 6 (1875); Ann. Chim. Phys. (6), 25, 226 (1892).

Other salts.TABLE XXXVI.—*Solubility of carbon dioxide in aqueous solutions of different salts.^a*

Composition of solution.	Temperature.	Solubility.
	° C.	
6.27 per cent Ba(NO ₃) ₂ solution.....	15.2	0.922
8.35 per cent Ba(NO ₃) ₂ solution.....	22.0	.715
4.10 per cent Ca(NO ₃) ₂ solution.....	15.2	.923
5.29 per cent Sr(NO ₃) ₂ solution.....	15.2	.916
12.8 per cent CaSO ₄ solution.....	18.38	.672
34 per cent AgNO ₃ solution.....	18.38	.648
11.9 per cent MgCl ₂ solution.....	22.4	.451

^a Setschenow, Mémoires de l'acad. impér. des sci. de St.-Petersb. (7), 22, No. 6 (1875).

GENERAL CONCLUSIONS.

The following general conclusions may be drawn from the work upon the solubility of carbon dioxide in various solutions:

1. The solubility in salt solutions is less than in an equal volume of water.

2. The solubility of carbon dioxide in water is increased by addition of nitric acid.

3. The solubility of carbon dioxide in sulphuric acid is decreased by the addition of water; likewise the solubility of carbon dioxide

in water is decreased by the addition of sulphuric acid; consequently there is a mixture of sulphuric acid and water, which dissolves a minimum quantity of carbon dioxide.

4. The more concentrated the solutions are, the less carbon dioxide is absorbed.

5. The solubility in solutions of strontium chloride is between that in calcium and barium chlorides.

6. The quantity of carbon dioxide absorbed becomes less as the temperature increases.

7. The solubility is less in sulphate solutions than in chloride solutions, and less in chloride solutions than in nitrate solutions.

8. Solutions of sodium salts absorb carbon dioxide less readily than solutions of similar potassium salts, and solutions of ammonium salts are better solvents than solutions of either sodium or potassium salts.

LIME.

SOLUBILITY OF LIME IN WATER.

Many experimenters have investigated the solubility of lime in water at different temperatures, and on account of the many precautions which must be taken in such determinations the results have not shown a satisfactory agreement. It is essential that the water in which the lime is to be dissolved should be absolutely free from impurities, especially materials of organic origin, which will be shown to possess a very great solvent action on lime. It is also essential in any accurate determinations that the source and impurities of the lime should be known. That there is a difference in the solubility of lime, depending on the source and consequently upon the impurities present, is seen from the determinations of Lamy^a upon lime obtained from different sources. These results are given in the following table:

TABLE XXXVII.—*Solubility of lime obtained from different sources.*

Temperature.	Lime in 1,000 parts of solution.		
	From nitrate.	From marble.	Hydrate.
° C.	Parts.	Parts.	Parts.
0	1.362	1.281	1.430
10	1.311	1.342	1.284
15	1.277	1.299	1.344
30	1.142	1.162	1.195
45	.996	1.005	1.033
60	.864	.868	.885
100	.562	.576	.584

^a Compt. rend., 86, 333 (1878).

The solubility of lime in water at different temperatures has been investigated by many experimenters ^a and the results of these investigations have been collected in the following table and the accompanying plate:

TABLE XXXVIII.—*Solubility of lime (CaO) in water.*

[Given in grams per liter.]

Temp.	Dalton.	Phillips.	Carles.	Pavesi and Rotondi.	Witt- stein.	Tich- borne.	Maben.
°C.							
0							1.318
5							1.309
10							1.298
13				1.274			
15							1.284
15.6	1.29	1.29			1.37	1.35	
19			1.251	1.241			1.264
20							
23				1.228			
25							1.203
30							1.160
35							1.100
40							1.073
45							1.015
50							.982
54.4	1.03						
55							.906
60							.880
65							.828
70							.810
75							.763
80							.734
85							.720
90							.633
95							.606
99							
100	.789				.752	.747	.606
109						.560	
120							
150							
190							

^aDalton, *New System of Chemical Philosophy*, Manchester (1808), cited by Phillips, *Ann. Chim. Phys.* (2), **16**, 213 (1821); Carles, *Pharm. Jour. Trans.* (3), **4**, 550 (1874); Pavesi and Rotondi, *Ber. deutsch. chem. Ges.*, **7**, 817 (1874); Wittstein, *Repert. Pharm.* (3), **1**, 182 (1848); Boutron and Boudet, *Jour. Pharm.* (3), **26**, 16 (1854); Tichborne, *Chem. News*, **24**, 199 (1871); Maben, *Pharm. Jour. Trans.* (3), **14**, 505 (1883); Lunge, *Jour. Soc. Chem. Ind.*, **11**, 882 (1892); Cabot, *ibid.*, **16**, 417 (1897); Herzfeld, *Bied. Centr.*, **27**, 571 (1898); Guthrie, *Jour. Soc. Chem. Ind.*, **20**, 223 (1901); Herold, *Zeit. Elektrochem.*, **11**, 417 (1905); Tilden and Shenstone, *Proc. Roy. Soc.*, **38**, 33 (1885).

TABLE XXXVIII.—*Solubility of lime (CaO) in water*—Continued.

[Given in grams per liter.]

Temp.	Lunge.	Cabot.	Herzfeld.	Guthrie.	Herold.	Tilden and Shenstone.
° C.						
0		1.36				
5				1.350		
10				1.342		
13						
15		1.31	1.29	1.320		
15.6						
19						1.182
20	1.374		1.23	1.293		
23						
25			1.18	1.254		
30			1.13	1.219		
35			1.08	1.161		
40	1.162		1.04	1.119		
45			.996			
50			.958	.981		
54.4						
55			.902			
60	1.026		.864	.879		
65			.801			
70			.752	.781		
75			.709			
80	.845		.675	.740		
85						
90				.696		
95						
99		.635				
100	.664			.597		
109						
120					0.305	
150					.169	.246
190					.084	

In spite of the lack of satisfactory accord between these various determinations, the results indicate that lime is about twice as soluble^a at 0° as it is at 100° C., and that the solubility curve approximates a straight line between the temperatures 25° and 100° C. (See figure 1.)

SOLUBILITY OF LIME IN AQUEOUS SOLUTIONS.

Ammonium chloride.

There are many qualitative statements in the literature that lime is much more soluble in ammonium chloride solutions than in water. The quantitative results obtained by Noyes and Chapin^b are given in the following table:

TABLE XXXIX.—*Solubility of lime in ammonium chloride solutions at 25° C.*

Ammonium chloride per liter.	Lime per liter.
<i>Grams.</i>	<i>Grams.</i>
0.0	1.134
1.164	1.631
2.328	2.201
4.655	3.348

^a This result is also given by Goldammer, Pharm. Centr., 26, 442, 455 (1885); abstr. in Jour. Soc. Chem. Ind., 5, 450 (1866).

^b Zeit. phys. Chem., 28, 518 (1899).

From this table it will be seen that by increasing the quantity of ammonium chloride in the solution the solubility of lime is also

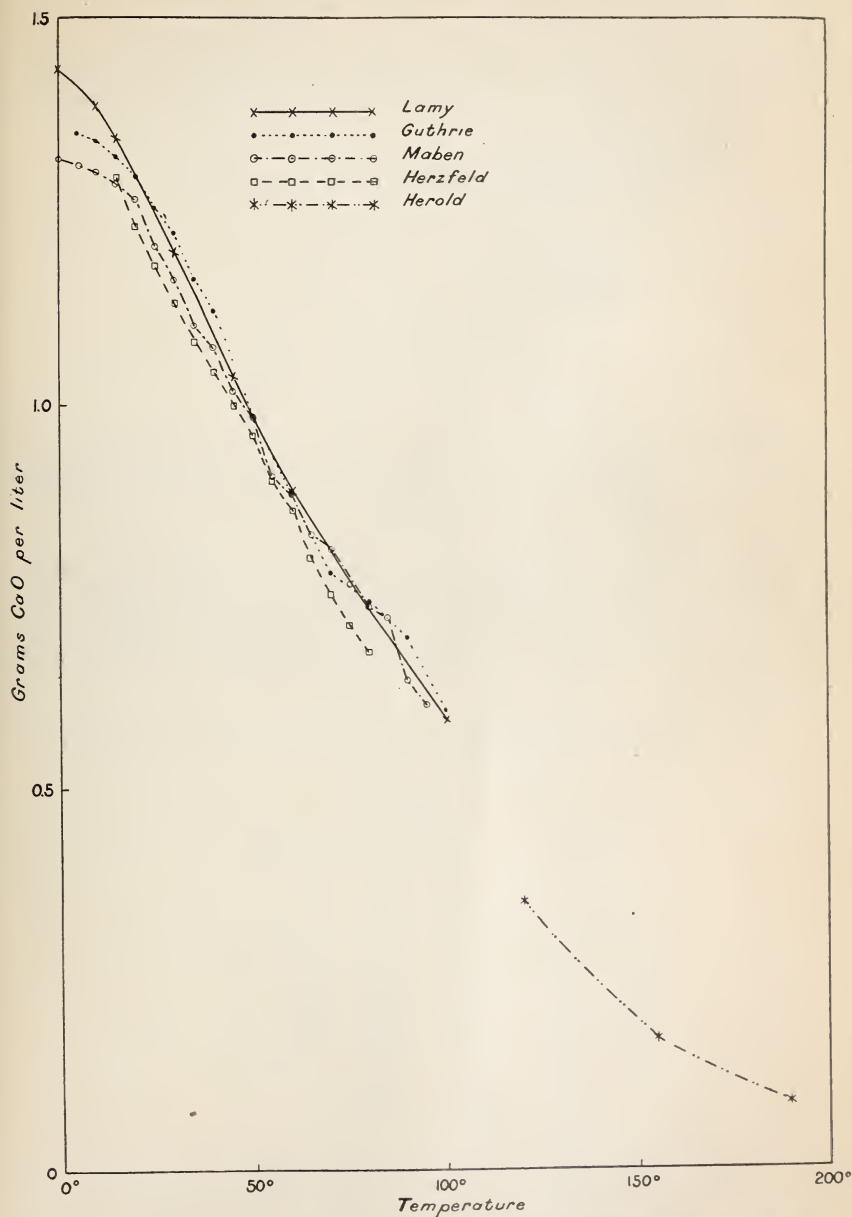


FIG. 1.—Solubility of lime in water at various temperatures according to various experiments.

increased, and at the concentrations employed the increase is nearly proportional to the concentration of ammonium chloride.

Sodium chloride.

Lime is more soluble in sodium chloride solutions than in pure water. According to Lunge,^a at 50° C. a sodium chloride solution (5 to 10 per cent) dissolves about 35 per cent more lime than does water at the same temperature. The solubility for different concentrations of sodium chloride at different temperatures has been given by Cabot^b as follows:

TABLE XL.—*Solubility of lime in sodium chloride solutions.*

NaCl per liter.	CaO per liter.		
	0° C.	15° C.	99° C.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
0	1.36	1.31	0.635
30	1.813	1.703	.969
60	-----	1.824	1.004
120	1.86	1.722	1.015
240	1.36	1.274	.771
Saturated.	1.054	.929	.583

With increase of sodium chloride in solution the solubility of lime increases to a maximum and then decreases again until the saturation point for sodium chloride is reached.

These results are confirmed by the experiments of Maigret^c upon the solubility of lime in sodium chloride solutions. The results also show that the presence of sodium hydroxide causes a decrease in the quantity of lime in solution. The following table gives the results of this work:

TABLE XLI.—*Solubility of lime in sodium chloride solutions containing various quantities of sodium hydroxide.*

NaCl per liter.	CaO per liter.		
	No NaOH.	0.8 gram NaOH per liter.	4.0 grams NaOH per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>
0	1.3	0.8	0.22
5	1.4	.9	-----
10	1.6	1.0	-----
25	1.7	1.1	-----
50	1.8	1.25	-----
75	1.9	1.4	.55
100	1.85	1.4	-----
125	1.7	1.3	-----
150	1.65	1.25	.44
175	1.6	1.2	-----
182	1.6	1.2	-----
200	1.55	1.1	-----
225	1.4	1.0	-----
250	1.3	.9	-----
275	1.2	.7	-----
300	1.1	.7	.22
314	1.0	-----	-----

^a Jour. Soc. Chem. Ind., **11**, 882 (1892).^b Jour. Soc. Chem. Ind., **16**, 417 (1897).^c Bul. Soc. Chim. (3), **33**, 631 (1905).

Potassium chloride.

According to Lunge,^a at 50° C. a potassium chloride solution (5 to 10 per cent) dissolves about 35 per cent more lime than does water at the same temperature. The solubility for different concentrations of potassium chloride at different temperatures has been given by Cabot^b as follows:

TABLE XLII.—*Solubility of lime in potassium chloride solutions.*

KCl per liter.	CaO per liter.		
	0° C.	15° C.	99° C.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>
0	1.36	1.31	0.635
30	1.701	1.658	.788
60	1.725	1.674	.876
120	1.718	1.606	.894
240	1.248	1.199	.612
Saturated.	1.21	-----	-----

The solubility increases with increase of potassium chloride to a maximum and then decreases again as the concentration of potassium chloride approaches the saturation point.

Calcium chloride.

It might be expected that the solubility of lime in the solution of a salt yielding a common ion would be depressed. There are indications that this actually happens at lower temperatures and in the more dilute solutions of calcium chloride. In the more concentrated solutions, however, this solubility is augmented, as will be observed from the following table by Lunge^b and Zahorsky.^c

TABLE XLIII.—*Lime dissolved at different temperatures by various solutions of calcium chloride.*

CaCl ₂	CaO per 100 c. c. solution.				
	20° C.	40° C.	60° C.	80° C.	100° C.
<i>Per cent.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
0	9.1374	0.1162	0.1026	0.0845	0.0664
5	.1370	.1160	.1020	.0936	.0906
10	.1661	.1419	.1313	.1326	.1389
15	.1993	.1781	.1706	.1736	.1842
20	<i>a</i> 1857	.2249	.2204	.2295	.2325
25	<i>a</i> , 1661	<i>a</i> 3020	.2989	.3261	.3710
30	<i>a</i> , 1630	<i>a</i> , 3684	.3664	.4122	.4922

a Oxychloride separated out.

Lunge has pointed out from these results that solutions up to 10 per cent calcium chloride at ordinary or slightly raised temperatures alter the solubility very little from that in pure water. At the higher temperatures the presence of calcium chloride increases the

^a Jour. Soc. Chem. Ind., **11**, 882 (1892). ^b Jour. Soc. Chem. Ind., **16**, 417 (1897).

^c Zeit. anorg. Chem., **3**, 34 (1893).

solubility of lime proportionately with the quantity of calcium chloride, except where the phenomenon is complicated by precipitation of the solid oxychloride. The changes in solubility due to changes of temperature are not so great as the changes consequent upon changes in concentration of calcium chloride.

The recovery of manganese peroxide in the Weldon process is brought about by the action of lime upon the manganous salts. The presence of considerable quantities of calcium chloride is essential, and according to Lunge the most natural explanation is that it serves as a solvent for lime, as lime is much more soluble in hot solutions of calcium chloride than in water. This increased solubility has been attributed to the formation of an oxychloride in solution. That this explanation is not sufficient follows from a consideration of the relative solubilities of the oxychloride and of lime. Of two substances which may separate out as solid phase under any conditions the stable solid is that one whose solubility in the liquid is least, or which, after the precipitation has taken place, leaves the solution least concentrated. As the oxychloride separates out at the higher concentrations, it follows that the content of free lime in the solution is less than if the solid phase had been calcium hydroxide. The increased solubility of lime in calcium chloride solutions of the higher concentrations can not therefore be satisfactorily explained on the ground of the formation of oxychloride in solution.

The crystalline precipitate obtained by heating lime in a concentrated solution of calcium chloride was first observed by Buchholtz^a and later by Tromsdorf.^a At first it was supposed to be a modification of lime, but Berthollet^a subsequently showed it to be a compound of lime with calcium chloride. The ratio of lime to calcium chloride has been definitely determined by many experimenters as three to one, but the number of molecules of water of crystallization has been variously determined. Rose,^b Ditte,^c and André^d have ascribed to it the formula $3\text{CaO}.\text{CaCl}_2.16\text{H}_2\text{O}$; Beesley^e has given it the formula $3\text{CaO}.\text{CaCl}_2.14\text{H}_2\text{O}$; while Rose,^f Precht,^g Grimshaw,^h and Zahorskyⁱ indicate the formula $3\text{CaO}.\text{CaCl}_2.15\text{H}_2\text{O}$.

This compound is formed in large quantities in the production of ammonia by the action of lime on ammonium chloride, and all the above work upon its composition has been upon the compound

^a See Berthollet, *Essai de Statique Chimique*, 1, 350.

^b Schweig, *Jour.*, 29, 155 (1820).

^c *Compt. rend.*, 91, 576 (1880).

^d *Compt. rend.*, 92, 1452 (1881); *Ann. Chim. Phys.* (6), 3, 66 (1884).

^e *Phar. Jour. Trans.*, 9, 568 (1850).

^f Schweig, *Jour.*, 29, 155 (1820).

^g See Zahorsky, *Zeit. anorg. Chem.*, 3, 34 (1893).

^h *Chem. News*, 30, 280 (1874).

ⁱ *Zeit. anorg. Chem.*, 3, 34 (1893).

obtained by dissolving lime in warm or hot concentrated calcium chloride solutions and allowing it to settle after filtration. Upon standing, large crystals of the oxychloride separate. These are decomposed by water and by alcohol. Ditte has shown that when the oxychloride is treated with water the solution contains all the calcium chloride and part of the lime, while the residue of lime remains as a fine powder. This decomposition does not take place at 10° C. after the solution has reached the concentration of 85 grams calcium chloride per liter. Alcohol acts similarly, and at 17° C. no decomposition occurs if the alcohol contains 130 grams calcium chloride per liter, but calcium oxychloride passes into solution unchanged. Zahorsky has also proved that sodium, potassium, and ammonium chlorides in solution all decompose the oxychloride of calcium, free lime being left as a fine powder. Glycerol, however, has no decomposing influence upon the oxychloride, but dissolves it readily in the cold, the solution undergoing no decomposition upon heating. When an equal volume of water is added to the solution in glycerol, decomposition takes place, lime separating.

Sodium and potassium hydroxides.

According to Pelouze^a 100 parts of a solution containing 1 part of sodium or potassium hydroxide dissolves not more than one fifty-thousandth of 1 part of lime.

The following results by d'Anselme^b prove that the solubility of lime in sodium hydroxide solutions decreases with increasing concentrations of the caustic alkali and also with rise in temperature:

TABLE XLIV.—*Solubility of lime in solutions of sodium hydroxide.*

NaOH per liter.	CaO per liter.			
	20° C.	50° C.	70° C.	100° C.
<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
0.0	1.17	0.88	0.75	0.54
0.4	.94	.65	.53	.35
1.6	.57	.35	.225	.14
2.67	.39	.20	.11	.05
5.0	.18	.06	.04	.01
8.0	.11	.02	.01	Traces.
20.0	.02	Traces.	.00	.00

^a Ann. Chim. Phys. (3), **33**, 5 (1851).

^b Bul. Soc. Chim. (3), **29**, 936 (1903).

Calcium sulphate.

The mutual solubility of gypsum in lime solutions and of calcium hydroxide in gypsum solutions has recently been determined at 25° C. in this laboratory by Cameron and Bell ^a with the following results:

TABLE XLV.—*Mutual solubility of gypsum and lime at 25° C.*

CaSO ₄ per liter.	CaO per liter.	Solid phase.
<i>Grams.</i>	<i>Grams.</i>	
0.000	1.166	Ca(OH) ₂ .
.391	1.141	Ca(OH) ₂ .
.666	1.150	Ca(OH) ₂ .
.955	1.215	Ca(OH) ₂ .
1.214	1.212	Ca(OH) ₂ .
1.588	1.222	Ca(OH) ₂ , CaSO ₄ . 2H ₂ O.
1.634	.939	CaSO ₄ . 2H ₂ O.
1.722	.611	CaSO ₄ . 2H ₂ O.
1.853	.349	CaSO ₄ . 2H ₂ O.
1.918	.176	CaSO ₄ . 2H ₂ O.
2.032	.062	CaSO ₄ . 2H ₂ O.
2.126	.000	CaSO ₄ . 2H ₂ O.

It will be seen from these results that with increasing lime content in the solution the solubility of gypsum is steadily depressed. With increasing amounts of gypsum in the solution the solubility of lime seems to be nearly the same as in pure water. These results have been recently confirmed by further work in this laboratory by Bell and Taber.

Calcium nitrate.

The following table by Cameron and Robinson ^b gives the content of free lime in various solutions of calcium nitrate at 25°.

TABLE XLVI.—*Solubility of lime in calcium nitrate solutions at 25°.*

Density $\frac{25^\circ}{25^\circ}$.	CaO as Ca(OH) ₂ .		Ca(NO ₃) ₂ .	
	In 100 c. c.	In 100 grams H ₂ O.	In 100 c. c.	In 100 grams H ₂ O.
<i>Grams.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Grams.</i>	<i>Grams.</i>
1.0249	0.095	0.096	3.35	3.38
1.0484	.105	.109	8.18	8.52
1.0940	.120	.125	12.91	13.42
1.1383	.170	.181	19.43	20.73
1.1840	.171	.187	26.49	28.98
1.2101	.180	.198	29.82	32.84
1.2287	.190	.212	32.97	36.83
1.2290	.191	.213	33.27	37.55
1.2541	.200	.224	35.87	40.25
1.2581	.203	.230	37.04	41.98
1.2826	.226	.260	40.88	47.00
1.2905	.229	.263	41.08	47.16
1.3337	.277	.332	48.99	58.67
1.3735	.346	.429	50.88	69.40
1.4195	.440	.545	63.93	83.03
1.4840	.331	.449	73.58	99.70
1.5330	.263	.371	81.91	115.50
1.5809	.203	.303	90.38	135.30
1.5842	.000	.000	91.84	139.30

^a Jour. Am. Chem. Soc., 28, 1220 (1906); Bul. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906).

^b Jour. Phys. Chem., 11, 273 (1907).

These results are plotted in the accompanying diagram (fig. 2), in which four distinct curves are seen. In order to determine the composition of the solid phases along each of these curves the triangular diagram method of Schreinemakers and Bancroft was employed, and the following table gives the composition of the solutions and of the corresponding solid phases with adhering mother liquor.

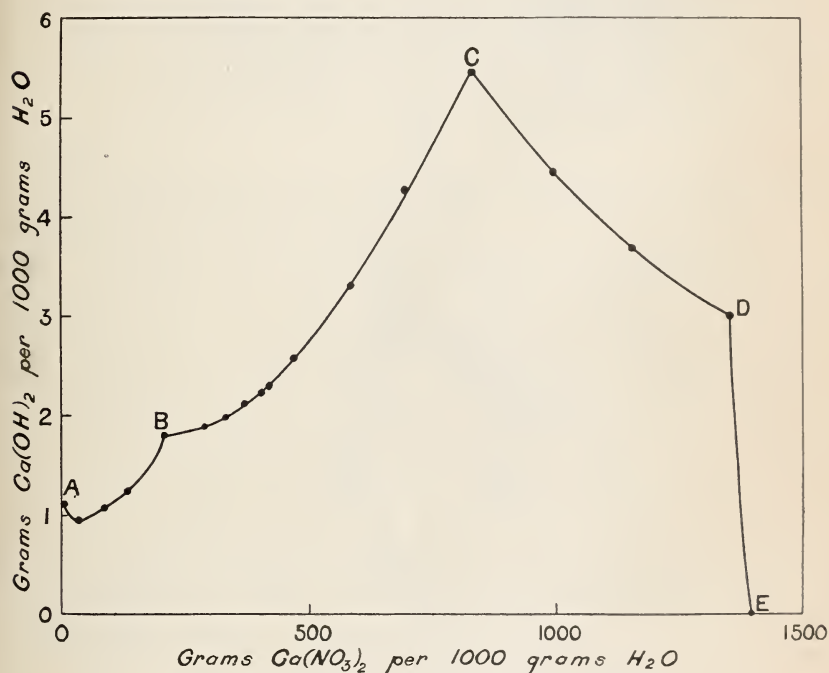


FIG. 2.—Solubility of lime in solutions of calcium nitrate at 25° C.

TABLE XLVII.—Composition of solutions and solid residues at 25°.

Point.	Solution.		Point.	Precipitate with adhering solution.	
	CaO.	N ₂ O ₅ .		CaO.	N ₂ O ₅ .
	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>
F.....	1.21	2.15	F'.....	40.85	1.00
G.....	4.16	7.80	G'.....	37.70	4.09
H.....	7.77	14.70	H'.....	33.26	7.20
I.....	9.34	17.84	I'.....	29.73	9.87
J.....	9.82	18.77	J'.....	27.49	11.60
K.....	14.21	26.87	K'.....	38.59	15.71
L.....	17.20	33.32	L'.....	31.64	36.36
M.....	18.50	35.33	M'.....	31.72	37.21

From the diagram (figure 3) it will be seen that the extension of the lines FF' and GG' meet in a point corresponding to solid calcium hydroxide. This substance, therefore, was the solid phase in contact with the solutions represented by the curve AB.

It is evident that the lines joining the points representing the composition of the solutions and their corresponding precipitates for the second branch of the curve, when extended, do not meet at a common point. The precipitate is therefore of variable composition, and since there can be only one solid phase present, it must be a series of solid solutions containing calcium oxide, nitric oxide, and probably water.

The residues along the third branch of the curve proved to be a substance occurring in long acicular crystals. As scaled off from the diagram its percentage composition is CaO, 39.5; N_2O_5 , 38.0, and

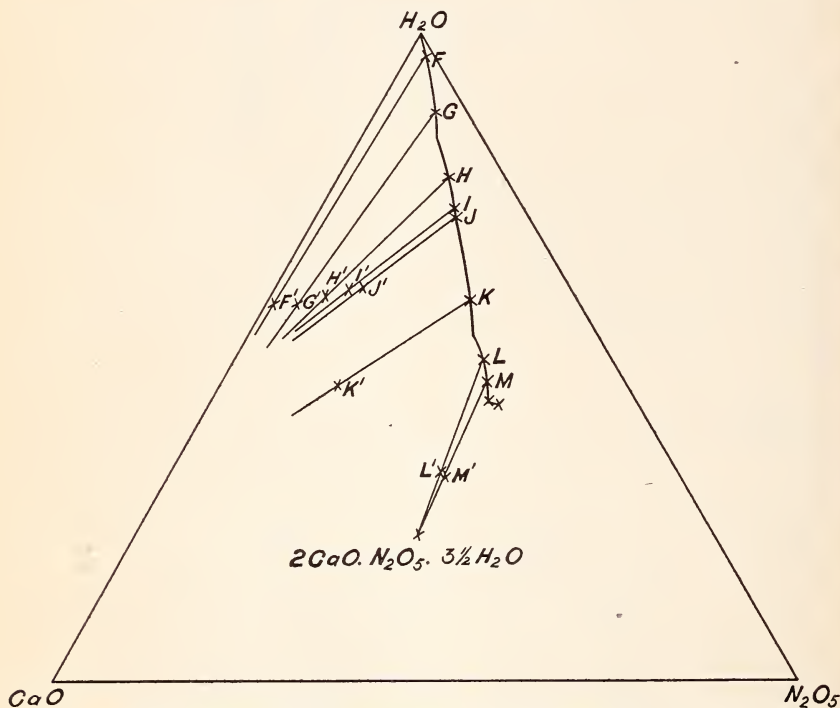


FIG. 3.—Triangular diagram showing the composition of the solutions and of the solid phases in contact with the solutions at 25° C., where there are present lime, calcium nitrate, and water.

H_2O , 22.5; corresponding to the compound $2\text{CaO}.\text{N}_2\text{O}_5.3\frac{1}{2}\text{H}_2\text{O}$, and is identical with the one described by Werner.^a

The solid phase in contact with the solutions along the fourth branch of the curve was undoubtedly the well-known normal nitrate $\text{Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$, and no further attempt was made to demonstrate its composition. The data for the "constant" solutions have been brought together in the following table:

^a Ann. Chim. Phys. (6), **27**, 570 (1892); Compt. rend., **115**, 169 (1892).

TABLE XLVIII.—Data for the “constant” solutions in the system, calcium nitrate, lime, and water at 25° C.

Points.	Solid phases in contact with solution.	Concentration of respective solutions; grams per 100 grams H ₂ O.	
		CaO as Ca(OH) ₂ .	Ca(NO ₃) ₂ .
A	Ca(OH) ₂	0.118	0.0
B	Ca(OH) ₂ , and solid solution (CaO.xN ₂ O ₅ .yH ₂ O).....	.170	20.73
C	Solid solution (CaO.xN ₂ O ₅ .yH ₂ O) and CaO.N ₂ O ₅ .3½H ₂ O.....	.440	83.03
D	CaO.N ₂ O ₅ .3½H ₂ O, and Ca(NO ₃) ₂ .4H ₂ O.....	.203	135.3
E	Ca(NO ₃) ₂ .4H ₂ O.....	.000	139.30

Glycerol.

The following table gives the results of Berthelot ^a upon the solubility of lime in glycerol solutions.

TABLE XLIX.—Solubility of lime in glycerol solutions at 5° C.

Glycerol per 100 c. c. solution.	CaO per 100 c. c. solution.
<i>Grams.</i>	<i>Gram.</i>
1	0.165
2	.186
2.50	.192
2.86	.196
5	.240
10	.370

The results of Carles ^b are in accord with these, showing that as the content of the solution in glycerol becomes greater, the solubility of lime also increases.

TABLE L.—Solubility of lime in glycerol solutions.

Solution containing—		CaO dissolved.
Water.	Glycerol.	
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1,000	0	1.251
1,000	50	1.865
1,000	100	2.583
1,000	200	4.040
1,000	400	6.569

The presence of glycerol in solution increases the solubility of lime, as the following table by Puls ^c indicates:

^a Ann. Chim. Phys. (3), **46**, 173 (1856). ^b Pharm. Jour. Trans. (3), **4**, 550 (1874).

^c Jour. prakt. Chem., **123**, 83 (1877).

TABLE LI.—*Solubility of lime in glycerol solutions.*

Glycerol per 100 grams solution.	CaO per 100 grams solution.	Glycerol per 100 grams solution.	CaO per 100 grams solution.
<i>Grams.</i>	<i>Gram.</i>	<i>Grams.</i>	<i>Grams.</i>
0.0	0.148	10.00	0.370
2.00	.186	26.97	.595
2.50	.192	37.91	.852
2.86	.196	51.15	1.434
5.00	.240		

The following table contains the results of Herz and Knoch: ^a

TABLE LII.—*Solubility of lime in glycerol solutions at 25° C.*

Density 25° 25°	Glycerol in solvent.	Ca(OH) ₂ per liter.
	<i>Per cent.</i>	<i>Grams.</i>
1.0003	0.0	1.59
1.0244	7.15	3.01
1.0537	20.44	4.51
1.0842	31.55	8.33
1.1137	40.95	14.80
1.1356	48.70	16.30
1.2072	69.20	35.40

Mannite.

In mannite solutions also Berthelot ^b has found that the solubility of lime is increased. The results are given in the following table:

TABLE LIII.—*Solubility of lime in mannite solutions at 5° C.*

Mannite per 100 c. c. solution.	CaO per 100 c. c. solution.	Mannite per 100 c. c. solution.	CaO per 100 c. c. solution.
<i>Grams.</i>	<i>Gram.</i>	<i>Grams.</i>	<i>Gram.</i>
0.0	0.148	1.37	0.194
.096	.154	1.60	.207
.192	.155	1.92	.225
.96	.186	2.40	.255
1.09	.190	4.80	.372
1.20	.193	9.60	.753

Sugar.

The use of lime to neutralize the acid employed in the settling tanks in sugar factories makes the subject of the solubility of lime in sugar solutions one of prime importance. Considerable work has been done on this subject and the results are not altogether concordant. Owing to the fact that sugar and lime form addition compounds the quantity of lime added to a given sugar solution should be taken into account, as the solid phase resulting contains considerable percentages of sugar. Several formulas have been ascribed to the double compound obtained by adding lime to sugar solutions at ordinary temperature. Péligot, ^c Soubeiran, ^d and Benedikt ^e have

^a Zeit. anorg. Chem., **46**, 193 (1905).

^b Ann. Chim. Phys. (3), **46**, 173 (1856).

^c Ann. Chim. Phys. (2), **67**, 113 (1838); Compt. rend., **32**, 333 (1851).

^d Jour. Pharm. (3), **1**, 469 (1842).

^e Ber. deutsch. chem. Ges., **6**, 413 (1873).

recorded the compound $C_{12}H_{22}O_{11} \cdot CaO$; Soubeiran found another compound, $2C_{12}H_{22}O_{11} \cdot 3CaO$; and Pélilot^a and Dubrunfaut^b have recorded the compound $C_{12}H_{22}O_{11} \cdot 3CaO$. The last author has also determined the ratio of lime to sugar in saturated solutions at different temperatures. The molecular ratio of lime to sugar is eight times as great at or below 0° as it is at 100° C. Pélilot^c has determined the composition of the solid phase in contact with a series of solutions in which the sugar content varies from 2.5 to 40 grams of sugar per 100 grams of water. The composition of the solid phase was found to vary continuously from 13.8 per cent to 21.0 per cent lime, thus indicating that lime and sugar form a series of solid solutions, of which the above recorded "compounds" are members. The so-called solubility of lime in sugar solutions is in fact, then, the quantity of lime in the sugar solution, the solid phase being one of the above described solid solutions. When these solids are heated with water the solutions cloud, as the quantity of lime in hot sugar solutions is very much less than in cold solutions. On cooling again the solutions clear up. The following results of Lamy^d show this to be the case in 10 per cent sugar solutions. The solubility in water at the same temperature has been given, and it will be seen that sugar increases the solubility much more in cold solutions than it does when the solutions are hot.

TABLE LIV.—*Solubility of lime in water and in 10 per cent sugar solutions.*

Temper- ature.	CaO per 1,000 grams 10 per cent sugar so- lution.	CaO per 1,000 grams water.
$^\circ$ C.	Grams.	Grams.
100	13.5	6.0
70	23.0	7.9
50	53.0	9.6
30	120.5	11.7

In the following table there have been recorded the results of Berthelot^e upon the solubility of lime in various sugar solutions:

TABLE LV.—*Solubility of lime in sugar solutions at 5° C.*

Sugar per 100 c. c. solution.	CaO per 100 c. c. solution.	Sugar per 100 c. c. solution.	CaO per 100 c. c. solution.
Grams.	Gram.	Grams.	Grams.
0.0	0.148	1.200	.316
.096	.154	1.386	.326
.191	.172	1.660	.364
.400	.194	2.000	.433
.960	.264	2.401	.484
1.058	.281	4.850	1.031

^a Jour. Pharm. (3), 19, 324 (1851).^b Compt. rend., 32, 498 (1851).^c Compt. rend., 32, 333 (1851).^d See Weisberg. Bul. Soc. Chim. (3), 23, 740 (1900).^e Ann. Chim. Phys. (3), 46, 173 (1856).

Weisberg^a has collected the data of several authors upon the solubility of lime in sugar solutions and has calculated the ratio of lime to sugar in the solution. Also in the following table are the results obtained by using different quantities of lime with which to saturate the solutions. In all probability the quantity of lime has caused a marked change in the quantity of sugar in the solution by the union of lime and sugar in the solid phase.

TABLE LVI.—*Solubility of lime in sugar solutions according to various authors.*

Berthelot.		Péligot.		Petit.		Schatten.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
0.400	48.50	2.33	16.00	1.71	16.4	1	29.10
.960	27.48	4.64	18.06	3.52	16.4	2	22.70
1.058	26.57	6.97	20.33	4.275	16.4	3	20.95
1.386	23.52	9.31	22.10	6.84	18.4	6	19.66
1.660	21.92	11.39	22.40	8.55	20.5	8	20.64
2.000	21.65	13.47	22.70	10.40	25.3	11	23.17
2.401	20.16	15.55	23.00	17.10	25.7	13	24.23
4.850	21.15	17.63	23.15	22.80	27.3	16	26.26
.....	21.32	24.69

TABLE LVII.—*Solubility of lime in sugar solutions according to Weisberg, showing the effect of adding lime in varying quantities.*

[T=16° C.]

CaO in excess.		CaO in great excess.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
0.7814	37.9	0.625	71.6
.912	32.3	.964	53.4
1.400	30.5	2.084	36.0
1.693	28.9	3.028	32.3
4.754	27.7	3.451	31.7
5.73	27.1	4.168	30.2
10.59	27.5	4.880	28.7
11.20	27.2	5.73	28.3
12.50	27.3	6.12	27.4
13.93	27.9	6.25	27.7
14.49	27.5	6.51	27.5
16.41	28.0	7.55	27.9
.....	8.20	27.3

The following table by Weisberg^b shows the different solubility of quicklime, of calcium hydroxide, and of slaked lime. The apparent difference may probably be ascribed to the nonattainment of equilibrium conditions.

^a Bul. Soc. Chim. (3), 21, 773 (1899).^b Bul. Soc. Chim. (3), 23, 740 (1900).

TABLE LVIII.—*Solubility of quicklime and of slaked lime in sugar solutions at 15° to 16° C.*

CaO.		Ca(OH) ₂ .		Ca(OH) ₂ +H ₂ O.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
13.00	27.75	13.00	25.40
11.34	27.57	11.96	25.45	11.18	22.40
10.30	27.87	10.87	25.40	10.40	22.90
9.67	27.61	9.67	25.00
8.27	27.49	8.90	24.74	8.68	22.80
7.64	27.50	8.06	24.72	7.28	21.70
6.84	27.42	6.97	24.50	6.29	20.90
5.77	27.80	5.46	24.50	5.22	20.55
4.73	27.90	4.52	24.23	4.03	20.60
3.95	27.73	3.56	23.60
3.02	27.78	2.57	23.40
2.29	27.93	1.85	23.30	2.91	20.05

Finally, Weisberg has compared the solvent action of hot sugar solutions on lime with that of cold sugar solutions.

TABLE LIX.—*Solubility of various samples of lime in hot and cold sugar solutions.*

CaO.				Ca(OH) ₂ .				Ca(OH) ₂ +H ₂ O.			
Ordinary temperature.		80° C.		Ordinary temperature.		90° C.		Ordinary temperature.		90° C.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
13.68	27.8	10.97	21.18	12.13	25.5	8.16	7.50
10.76	27.6	7.49	16.60	11.59	26.0	7.12	6.84	11.49	23.1	8.79	11.78
6.56	27.7	4.58	16.15	9.15	26.0	5.72	6.36	8.85	23.1	6.29	8.18
4.00	27.4	2.68	13.59	8.68	25.5	5.62	7.67	5.67	23.1	3.95	7.65
4.43	27.8	2.78	8.85

GENERAL CONCLUSIONS.

1. The apparent solubility of lime in aqueous solutions is greatly dependent on its origin, and therefore on the impurities it contains.

2. The solubility of lime at 0° C. is approximately twice its solubility at 100° C. The temperature-solubility curve approximates a straight line.

3. The solubility of lime in dilute solutions of the chlorides of sodium, potassium, and ammonium is greater than in pure water. The solubility curves for solutions of the chlorides of sodium and potassium have maximum points, and in saturated solutions the solubility is less than in pure water.

4. The solubility of lime in very dilute solutions of calcium chloride seems to be less than in pure water, but as the concentration increases the solubility is raised much above that in pure water, especially at higher temperatures.

5. At lower temperatures and in the more concentrated solutions of calcium chloride the stable solid phase is calcium oxychloride.

6. The presence of other hydroxides depresses markedly the solubility of lime.

7. The presence of gypsum does not appreciably affect the solubility of lime.

8. In contact with very dilute solutions of calcium nitrate, lime passes into solution as such, the solubility increasing with concentration of nitrate; at higher concentrations the stable solid is one of a series of solid solutions, the content of lime still increasing with increase of nitrate; at still higher concentrations the stable solid is a basic nitrate of definite composition, and the concentration of lime in solution falls with increase of nitrate; finally, at very high concentrations the neutral nitrate separates as a solid phase.

9. In solutions of glycerol or mannite the solubility of lime is increased markedly with increase of concentration of the carbohydrate.

10. When lime is brought into contact with sugar solutions the ratio of lime to sugar in the solid varies continuously with the composition of the solution, and consequently the solid compound resulting when lime is added in excess to a sugar solution is one of a series of solid solutions.

11. Cold sugar solutions have a much greater solvent action upon lime than have the same solutions when hot. Heating tends to precipitate one of the solid solutions described above.

12. The ratio of lime to sugar in solution depends on the temperature and on the concentration.

CALCIUM CARBONATE.

MODIFICATIONS OF CALCIUM CARBONATE.

The formation of carbonates in nature has been the subject of much research by chemical geologists.^a Two forms of calcium carbonate are common, calcite and aragonite, and there seems to be good reason for believing that at the higher temperatures and in salt solutions aragonite is the stable solid phase. Watson^b states that above 30° C. aragonite is the stable form of calcium carbonate in the presence of solutions of sodium chloride or ammonium chloride. Below that temperature, calcite is stable.

The experiments of Foote^c have shown that at ordinary temperatures calcite is the stable form of calcium carbonate in solutions of carbon dioxide and also in mixed solutions of potassium carbonate and oxalate. The solubility of calcite is shown by electrical con-

^a For a review of the literature see Vater, *Zeit. Kryst.*, **21**, 433 (1893).

^b *Chem. News*, **63**, 109 (1891).

^c *Zeit. phys. Chem.*, **33**, 740 (1900).

ductivity to be less than that of aragonite in carbon dioxide solutions. The conductivity of solutions saturated with carbon dioxide and calcium carbonate, either as calcite or aragonite, was measured at different temperatures. The following table gives the ratio of the conductivities.

TABLE LX.—*Ratio of conductivity of solutions of calcite and aragonite in water saturated with carbon dioxide.*

Tempera- ture.	Aragonite Calcite.
°C.	
8	1.147
25	1.130
41	1.124
48	1.115

It is apparent that the solubility of aragonite is higher than that of calcite, and therefore that calcite is the stable solid phase under these conditions. The ratio is smaller at higher temperatures, indicating that the solubility curves are approaching one another, and that at some higher temperature aragonite would probably become the stable phase. The effect of various salts has not been closely investigated.

A large amount of chemical work and of speculation has been done upon the conditions of the formation of dolomite in nature. The theory that dolomite resulted from the action of vapors of volcanic origin upon limestone rocks has long since been abandoned. All the authorities are now agreed that dolomite has been deposited from aqueous solution, either by deposition of the carbonates of calcium and magnesium together or by the action of water carrying magnesium salts on some form of calcium carbonate. In nearly all the experiments upon the artificial formation of dolomite high temperature has been necessary. By heating a solution of magnesium sulphate with calcium carbonate in a sealed tube to 200° C. von Morlot ^a has obtained dolomite; Favre ^b used a solution of magnesium chloride; Hoppe-Seyler ^c used a solution of magnesium sulphate and calcium carbonate saturated with carbon dioxide above 100° C., and also confirmed the results of von Morlot and of Favre. Hunt ^d mixed equivalent quantities of the chlorides of magnesium and calcium and added sodium carbonate to the solution. At high temperature dolomite was formed. In all the above work calcium carbonate in the form of calcite was employed. Klement ^e has investigated the

^a Haidinger's Naturwiss. Abhandl., **1**, 305 (1847).

^b Arch. Sci. Phys. et Nat., **10**, 177 (1849).

^c Zeit. deutsch. geol. Gesell., **27**, 495 (1875).

^d Am. Jour. Sci. (2), **28**, 170, 365 (1859); **42**, 49 (1866).

^e Bul. Soc. Belge. Geol., **8**, 219 (1894); Tschermaks Mitt., **14**, 526 (1895).

action of magnesium solutions upon aragonite under various conditions. He finds that at about 60° C. magnesium sulphate in saturated sodium chloride solutions begins to react upon aragonite to form dolomite, while under like conditions there is no reaction upon calcite. The extent of reaction increases with the time of contact, with the temperature, and with the concentration of salt in solution. There seems to be a maximum amount of magnesium carbonate in the solid for each temperature. At 91° C. 42 per cent of the solid is magnesium carbonate. The addition of the sodium chloride is equivalent to raising the temperature. In some further experiments coral was employed and was shown to act very similarly to aragonite. The final conclusion is that dolomite is formed by the action of sea water on aragonite, hot and in concentrated solution. Pfaff^a has shown that dolomite separates from solution saturated with common salt, the carbonates of lime and magnesium, and carbon dioxide, in the presence of sulphides. The sulphides are derived in nature by the action of organic materials upon sulphates.

HYDRATES OF CALCIUM CARBONATE.

Rammelsberg^b found in a river rhomboidal crystals of $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$, which at 15° C. were dehydrated even under water. Pelouze^c has obtained the same compound by exposing a solution of lime in sugar at a temperature of 7° to 8° C. After some weeks the above compound was formed. At a lower temperature $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ was produced when carbon dioxide was passed into the solution. This same precipitate was obtained by passing carbon dioxide into lime water at 0° , the precipitate being at first flocculent but soon changing to a heavy crystalline powder. The crystals change at 30° C. to a semi-fluid paste, which is a mixture of anhydrous calcium carbonate and water, a result which was confirmed by Hunt.^d At 20° C. the same change occurs, but not so rapidly, and at lower temperatures the salt effloresces. At 0° the precipitate formed by mixing solutions of calcium chloride and sodium carbonate becomes crystalline on standing. Tschirwinsky^e considers that the existence of the hydrate $\text{CaCO}_3 \cdot 3\text{H}_2\text{O}$ has also been established and proposes the name *trihydrocalcite*.

SOLUBILITY OF CALCIUM CARBONATE IN WATER.

The results obtained by various experimenters on the solubility of calcium carbonate in water are far from concordant. In all likelihood this may be ascribed to impurities in the calcium carbonate—as, for instance, free lime would tend to increase the apparent solubility, if

^a N. Jahresb. f. Min., Beilage Bd. 9, 485 (1894).

^b Ber. deutsch. chem. Ges., 4, 469 (1871).

^c Jour. Pharm. (4), 1, 278 (1865).

^d Am. Jour. Sci. (2), 42, 49 (1866).

^e Annuaire géol. et minéral. Russie, 8, 245 (1906).

the calcium in solution was determined. Another reason is probably the presence of carbon dioxide in the water used by the early experimenters. Whipple and Mayer have more recently pointed out a very important source of error which has been almost disregarded by previous workers. The solubility of the glass vessels in water is sometimes much greater than that of the calcium carbonate, and these authors have tested this point by using glass of various kinds, and have found that Bohemian glass gave alkaline solutions which would have caused errors in solubility determinations of over 100 per cent. Jena glass they have found to be much more resistant to the action of water and have used this in their determinations, in which corrections have been made for the solubility of the glass vessels.

TABLE LXI.—*Solubility of calcium carbonate in water according to various experimenters.*

CaCO ₃ per liter.	Temperature.	Observer.
<i>Milligrams.</i>	<i>°C.</i>	
63	Brandes. ^a
42-63	Buchholz. ^a
113	(Hot)	Fresenius. ^b
94	(Cold)	Fresenius.
20	Péligot. ^c
78	15	Kremers. ^d
16	Bineau. ^e
34	Hofmann. ^f
36	Weitzien. ^g
34	Chevalet. ^h
13.1	16	Schloesing. ⁱ
28.5	Anderson. ^j
27	Lubavin. ^k
10	8.7	Hollemann. ^l
12.5	23.7	Hollemann.
103	12	Pollacci. ^m
145	100	Pollacci.
12.8	18	Le Blanc and Novotný. ⁿ
20.7	95 to 100	Le Blanc and Novotný.
13	20	Whipple and Mayer. ^o

^a See Comey, Dictionary of Chemical Solubilities (1896), 82.

^b Ann. Chem. Pharm., **59**, 177 (1846).

^c Jour. Pharm. (3), **19**, 324 (1851).

^d Ann. Phys. Chem., **85**, 246 (1852).

^e Ann. Chim. Phys. (3), **51**, 290 (1857).

^f Jour. Chem. Soc., **4**, 381 (1852).

^g Ann. Chem., **136**, 165 (1865).

^h Bul. mens. de la soc. chim. de Paris, Aug. 1868, p. 90; abstr. in Zeit. anal. Chem., **8**, 91 (1869).

ⁱ Compt. rend., **74**, 1552 (1872).

^j Proc. Roy. Soc. Edinburgh, **16**, 319 (1889).

^k Jour. Russ. Chem. Soc., **24**, 389 (1892); abstr. in Jour. Chem. Soc., **64** II, 373 (1893).

^l Zeit. phys. Chem., **12**, 125 (1893).

^m L'Orosi, **19**, 217 (1896); abstr. in Jour. Chem. Soc., **72** II, 260 (1897).

ⁿ Zeit. anorg. Chem., **51**, 181 (1906).

^o Jour. Infectious Diseases, Suppl. No. 2, 151 (1906).

SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS.

Carbon dioxide.

It was shown by Vogel^a as early as 1814 that when carbon dioxide is passed into lime water all the lime dissolves and when the solution is heated calcium carbonate precipitates. Upon the addition of carbon dioxide to the solution again the precipitate redissolves. The experiments by Irving^b indicate that heat is evolved both when

^a Bul. Pharm., **6**, 258 (1814).

^b Chem. News, **63**, 192 (1891).

the carbonate is being precipitated from lime water and also when the excess of carbon dioxide is redissolving the precipitate. The solubility of calcium carbonate in carbon dioxide solutions has been determined by many investigators and the early results are not at all concordant. The following table contains the results obtained by the various observers:

TABLE LXII.—*Solubility of calcium carbonate in water carrying carbon dioxide.*

CaCO ₃ per liter.	Temperature.	Observer.
<i>Grams.</i>	<i>°C.</i>	
0.7003.....	0	Lassaigne. ^a
.8803.....	10	Lassaigne.
.6700.....		Bergmann. ^b
1.800 (burnt lime).....		Bischof. ^c
2.800 (pure lime).....		Bischof.
2.500.....		Marchand. ^b
1.0 to 1.5.....		Struve. ^b
3.0.....		Caro. ^b
1.165 to 2.305.....		Boutron and Boudet. ^d
0.9842.....	12	Warrington. ^e
1.13 to 1.17.....	15	Treadwell and Reuter. ^f
1.30 to 1.31.....	13.2	Treadwell and Reuter.
1.43.....	28	Treadwell and Reuter.

^a Jour. Chim. Méd. (3), 4, 312 (1848).

^b See Caro, Inaug.-Diss., Jena (1873); Arch. Pharm. (3), 4, 145 (1874).

^c See Treadwell and Reuter, Zeit. anorg. Chem., 17, 170 (1898).

^d Jour. Pharm. (3), 26, 16 (1854).

^e Jour. Chem. Soc., 19, 296 (1866).

^f Zeit. anorg. Chem., 17, 170 (1898).

The above results show that the solubility depends very largely upon the purity of the original material. The solubility of calcium carbonate in water containing carbon dioxide is quite similar in kind to the solubility of dicalcium phosphate in phosphoric acid. Just as the amount of dicalcium phosphate in phosphoric acid solutions increases with increasing concentrations of acid,^a so the amount of calcium carbonate in carbon dioxide solutions increases with increasing amounts of carbon dioxide. The difference between the two cases is that in one instance the solid phase changes above certain concentrations of the acid in solution while in the case of the carbonate no carbonate other than CaCO₃ has been recorded. The results of Schloesing^b on the solubility of calcium carbonate in carbonic acid solutions at 16° C. are as follows:

^a See Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. (1907).

^b Compt. rend., 74, 1552 (1872).

TABLE LXIII.—*Solubility of calcium carbonate in water containing carbon dioxide at various partial pressures at 15° C.*

Pressure CO ₂ .	CO ₂ per liter.	CaCO ₃ per liter.
<i>Atmosphere.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
0.000504	60.96	74.6
.000808	72.11	85.0
.0033	123.0	137.2
.01387	218.36	223.1
.0282	310.4	296.5
.05008	408.5	360.0
.1422	-----	533.0
.2538	1,072.2	663.4
.4167	1,500.5	787.5
.5533	1,846.3	885.5
.7297	2,269.3	972.0
.9841	2,864.2	1,086.0

In a later paper^a Schloesing has shown that the equation $p^m = ky$ describes the results. In the equation p is the pressure of CO₂, y is the amount of bicarbonate in solution, i. e., the amount of CaO calculated as CaH₂(CO₃)₂, and m and k are constants.

The empirical formula of Schloesing has been modified by van't Hoff^b to the form $C_1^{2.56} = KC_2$, where C_1 is the concentration of calcium bicarbonate and C_2 is the concentration of carbon dioxide, which in turn is proportional to the partial pressure of the gas. The coefficient 2.56 is known as the "activity coefficient," and is shown to vary with the dilution and at very extreme dilution equals 3. Bodländer^c has calculated the dissociation constants at different dilutions and has recalculated Schloesing's results by a new formula, which describes the facts quite satisfactorily.

Where p is the pressure in atmospheres and y is the quantity of calcium bicarbonate in grams, the values of the constants are $m = 0.3787$ and $k = 0.9213$. Engel^d has determined the solubility of calcium carbonate at pressures greater than 1 atmosphere and has found that the formula proposed by Schloesing describes the conditions up to 6 atmospheres, which was the highest pressure at which he worked.

TABLE LXIV.—*Solubility of calcium carbonate in water containing carbon dioxide at higher pressures.*

Pressure CO ₂ .	CaCO ₃ per liter, ob- served.	CaCO ₃ per liter, calcu- lated.
<i>Atmospheres.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
1	1,079	1,085
2	1,403	1,411
4	1,820	1,834
6	2,109	2,139

^a Compt. rend., **75**, 70 (1872).^b Vorlesungen über theoretische und physikalische Chemie, I, 149.^c Zeit. phys. Chem., **35**, 23 (1900).^d Compt. rend., **101**, 949 (1885); Ann. Chim. Phys. (6), **13**, 344 (1888).

Treadwell and Reuter^a have also determined the solubility of calcium carbonate in solutions of carbon dioxide at temperatures 10° to 14° C. (average 12°), with the following results:

TABLE LXV.—*Solubility of calcium carbonate in various solutions of carbon dioxide in water.*

Pressure of CO ₂ .	CO ₂ per 100 c. c.	CaH ₂ (CO ₃) ₂ per 100 c. c.
<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
67.9	157.4	187.2
45.9	86.3	175.5
41.4	52.8	159.7
16.6	48.5	154.0
14.4	34.7	149.2
13.1	24.3	133.1
6.0	14.5	124.9
3.1	4.7	82.1
1.9	2.9	59.5
.6	-----	40.2

The quantity of various samples of calcium carbonate which sea water would dissolve under various pressures has been determined by Reid.^b In all the experiments the water contained about 1 gram of carbon dioxide per liter and the time of contact of the water and carbonate was 30 to 60 minutes.

TABLE LXVI.—*Solubility of calcium carbonate in water containing carbon dioxide.*

Material.	CO ₂ per liter sea water.	Pressure.	Temper- ature.	CaCO ₃ per liter.
	<i>Grams.</i>	<i>Tons.</i>	<i>° C.</i>	<i>Gram.</i>
Globigerina ooze I.....	1.0071	4	12.0	0.0906
	1.0494	4	12.0	.1486
	1.0523	4	9.0	.1191
	1.0203	4	9.0	.1080
	1.0102 (1 atm.)		12.2	.0568
	1.0744 (1 atm.)		10.0	.0572
Globigerina ooze II.....	1.0777	2	8.3	.0999
	1.0275	4	8.6	.0761
	1.0688	4	8.8	.0997
	1.0001 (1 atm.)		15.0	.0236
	1.0039 (1 atm.)		13.2	.0270
	1.0664	4	8.8	.1398
Coral sand I.....	1.0115	4	8.8	.1011
	1.0405 (1 atm.)		11.6	.0429
	1.0069 (1 atm.)		10.5	.0418
	.9666 (1 atm.)		12.2	.0407
Coral sand II.....	1.0596	4	9.1	.1220
	1.0738 (1 atm.)		9.0	.0391
Pteropods.....	1.0779	4	8.3	.1098
	1.0557 (1 atm.)		11.0	.0516
Crystalline.....	1.0307	4	8.3	.0371
	.9865	4	9.0	.0132
	.9845	(1 atm.)	10.0	.0102
	1.0410	-----	12.2	.0082
	1.0513	-----	12.2	.0050
	1.0440	-----	13.1	.0034
Ground crystals.....	1.0532	-----	14.7	.0045
	1.0536	-----	12.6	.0322

The author draws the conclusion that "the amount of carbonate of lime dissolved at a pressure of 4 tons per square inch is so much greater than the amount dissolved at the ordinary pressure that I think it

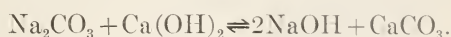
^a Zeit. anorg. Chem., **17**, 170 (1898).

^b Proc. Roy. Soc. Edinburgh, **15**, 151 (1888).

justifies the conclusion that the effect of pressure is to increase the rate of solution It is to be noted that, although these results may indicate that the solution of carbonate of lime in carbonic-acid water is more rapid under high pressures, it by no means follows that the solubility is *greater* than at the ordinary pressure (*ceteris paribus*)."

Sodium hydroxide and carbonate.

In the process of manufacture of caustic alkali from alkaline carbonate and lime the relative solubility of lime and of calcium carbonate in solutions of the alkalies and alkaline carbonates is an important factor in determining the equilibrium conditions. The caustification of sodium carbonate would be represented by the reaction,



This is a four-component system, water being the fourth component, and consequently when the temperature is fixed there may be five phases at some definite concentration. There may be four phases over a range of conditions, i. e., the system is univariant. Several experimenters have found the equilibrium conditions where there are the two solid phases—calcium hydroxide and calcium carbonate—liquid and vapor.

The presence of the reaction product, caustic soda, in solution depresses very greatly the solubility of calcium hydroxide, and consequently is one factor tending to bring the reaction to a standstill. Reference has already been made ^a to the results of d'Anselme on the solubility of lime in solutions of caustic soda.

As the solubility of calcium carbonate in sodium hydroxide solutions has been found to be less than in pure water, for dilute solutions of the alkali, this fact would tend to cause the reaction to go to the right, i. e., toward the formation of calcium carbonate and sodium hydroxide. The following results by Le Blanc and Novotný^b give the solubility of calcium carbonate in these solutions:

TABLE LXVII.—*Solubility of calcium carbonate in solutions of sodium hydroxide.*

NaOH per liter.	CaCO ₃ per liter.	
	80° C.	95° to 100° C.
<i>Gram.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
0.0	12.8	20.7
.004	8.7	9.6
.04	4.2	6.9
.4	4.3	5.7

^a Page 27.

^b Zeit. anorg. Chem., 51, 181 (1906).

The equilibrium conditions have been found experimentally by Lunge and Schmid,^a by Böldander and Lucas,^b and by Le Blanc and Novotný,^c all of whom have shown that the change from sodium carbonate to sodium hydroxide is much more complete in dilute solutions than in concentrated solutions. For instance, the last-named authors have determined the composition of the two sodium compounds present in the solution after an excess of lime has been added to varying solutions of sodium carbonate. At 100° C., when a normal solution was used, about 99 per cent of the sodium was present as sodium hydroxide, while when a 3-normal (3N) solution was used 93.6 per cent was present as hydroxide.

A recently published paper by Wegscheider^d contains an investigation of the nature of the solids formed when calcium carbonate is mixed with solutions of sodium carbonate. Above certain concentrations it was found that a double compound of sodium and calcium carbonate was formed, $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$ at 11° C., while at and above 40° C. the double compound was of the composition $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$. The following table gives the composition of the "constant" solutions at various temperatures, the concentration with regard to calcium carbonate being too small for determination:

TABLE LXVIII.—The "constant" solutions at various temperatures in the system, Na_2CO_3 , CaCO_3 , H_2O .

Temperature.	Solid phases.	Concentration of solution.
° C.		
11	CaCO_3 ; $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$	0.86 normal Na_2CO_3 .
40	CaCO_3 ; $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	2.14 normal Na_2CO_3 .
60do	3.77 normal Na_2CO_3 .
80do	4.34

The same author has also published results upon the equilibria obtaining when free caustic soda is present in the solution.

TABLE LXIX.—Solid phases at different concentrations and temperatures in the system, Na_2CO_3 , NaOH , CaCO_3 , H_2O .

Temperature.	Solid phases.	Concentration of solution.	
		Na_2CO_3 .	NaOH .
° C.			
60	CaCO_3 ; $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	1.8 normal....	2.6 normal.
60do	3.7 normal....	1.3 normal.
80do	1.9 normal....	2.9 normal.
80do	3.3 normal....	2.0 normal.

^a Ber. deutsch. chem. Ges., **18**, 3286 (1885).

^b Zeit. Elektrochem., **11**, 186 (1905); Zeit. angew. Chem., **13**, 1127 (1905).

^c Loc. cit.

^d Ann. Chem., **351**, 87 (1907).

Sodium chloride.

Lubavin^a has recorded the following qualitative result: 100 parts of a solution of sodium chloride (2.535 per cent) dissolves 0.0037 part CaCO_3 , calculated as CaO , or 0.0053 part calc-spar.

In the following experiments Cantoni and Goguelia^b have determined the quantity of calcium carbonate in solutions of sodium chloride after the solution had stood in contact with solid calcium carbonate for 98 days at room temperature (12° to 18°C.).

TABLE LXX.—*Solubility of calcium carbonate in sodium chloride.*[Time of contact, 98 days, at 12 to 18°C.]

NaCl in solution.	CaCO_3 per liter.
<i>Per cent.</i>	<i>Gram.</i>
5.85	0.0497
10.00	.0563
20.00	.0713

In the following experiments by Cameron, Bell, and Robinson^c carbon dioxide was carefully excluded by using distilled water which had been boiled for some time before the solutions were made. This was necessary, for carbon dioxide, even at a partial vapor pressure equal to that in the ordinary air, is capable of producing a great increase in the solubility in sodium chloride solutions.

TABLE LXXI.—*Solubility of calcium carbonate in sodium chloride solutions free from carbon dioxide at 25° .*

Density $\frac{25^\circ}{25^\circ}$	NaCl in 100 grams H_2O .	CaCO_3 in 100 grams H_2O .
	<i>Grams.</i>	<i>Gram.</i>
1.0079	1.601	0.0079
1.0314	5.177	.0086
1.0466	9.25	.0094
1.0734	11.48	.0104
1.0944	16.66	.0106
1.1346	22.04	.0115
1.1794	30.50	.0119

Sodium chloride and carbon dioxide.

In the following tables are given the results of Treadwell and Reuter,^d upon the solubility of calcium carbonate in water containing 5 grams of sodium chloride per liter and containing various quantities of carbon dioxide.

^a Jour. Russ. Phys. Chem. Soc., **24**, 389 (1892); abstr. in Jour. Chem. Soc., **64** ii, 373 (1893).

^b Bul. Soc. Chem. (3), **33**, 13 (1905).

^c Jour. Phys. Chem., **11**, 396 (1907).

^d Zeit. anorg. Chem., **17**, 170 (1898).

TABLE LXXII.—*Solubility of calcium carbonate in various solutions of carbon dioxide in sodium chloride solution ($\frac{1}{2}$ per cent).*

Pressure of CO ₂ .	CO ₂ per 100 c. c.	CaH ₂ (CO ₃) ₂ per 100 c. c.
<i>Millimeters.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
128.8	132.5	218.4
78.2	110.1	149.2
46.1	23.5	149.2
24.0	12.5	118.3
3.8	8.7	73.9
3.4	.3	49.0

By comparison with Table LXV it is apparent that the quantity both of free carbon dioxide and of calcium bicarbonate is less in salt solution than in pure water.

The following results are quoted from the work of Cameron and Seidell ^a upon the solubility of calcium carbonate in solutions of sodium chloride, the partial pressure of carbon dioxide in the vapor phase being that of ordinary air.

TABLE LXXIII.—*Solubility of calcium carbonate in aqueous solutions of sodium chloride at 25° C. in equilibrium with atmospheric air.*

NaCl per liter.	Calcium in so- lution, calcu- lated as CaH ₂ CO ₃ per liter.
<i>Grams.</i>	<i>Gram.</i>
0.0	0.1046
9.72	.1770
21.01	.2051
30.30	.2152
50.62	.2252
69.37	.2212
98.4	.2172
147.4	.1971
234.5	.1569
262.3	.1227

Table LXXIV gives the results where the pressure of the vapor phase, which consisted entirely of carbon dioxide and water vapor, was one atmosphere. This was attained by saturating the solutions with carbon dioxide at a lower temperature than 25° C. and removing the stopper of the bottles at intervals to allow the excess of the gas to escape after the bottles had been brought to the temperature of the experiment.

^aBul. No. 18, Division of Soils, U. S. Dept. Agr. (1901), p. 58; Jour. Phys. Chem., **6**, 50 (1902).

TABLE LXXIV.—*Solubility of calcium carbonate in sodium chloride solutions saturated with carbon dioxide at 25° C. and one atmosphere pressure.*

Density 25° 25°	NaCl in 100 grams H ₂ O.	CaCO ₃ in 100 grams H ₂ O.
	<i>Grams.</i>	<i>Gram.</i>
1.0129	1.45	0.150
1.0499	5.69	.160
1.0501	6.48	.173
1.0759	11.06	.174
1.1015	15.83	.172
1.1246	19.62	.159
1.1789	29.89	.123
1.1957	35.85	.103

Sodium sulphate.

The following experiments were similar to those in Table LXXI, except that sodium sulphate was used instead of sodium chloride.

TABLE LXXV.—*Solubility of calcium carbonate in sodium sulphate solutions free from carbon dioxide at 25° C.*

Density 25° 25°	Na ₂ SO ₄ in 100 grams water.	CaCO ₃ in 100 grams H ₂ O.
	<i>Grams.</i>	<i>Gram.</i>
1.0081	0.97	0.0151
1.0161	1.65	.0180
1.0363	4.90	.0262
1.1084	12.69	.0313
1.1200	14.55	.0322
1.1539	19.38	.0346
1.1615	21.02	.0343
1.1837	23.90	.0360

Sodium sulphate and carbon dioxide.TABLE LXXVI.—*Solubility of calcium carbonate in aqueous solutions of sodium sulphate at 24° C. in equilibrium with atmospheric air.*

Na ₂ SO ₄ per liter.	Total calcium calculated as CaH ₂ (CO ₃) ₂ per liter.	Calcium actu- ally dissolved, as CaH ₂ (CO ₃) ₂ per liter.
<i>Grams.</i>	<i>Gram.</i>	<i>Gram.</i>
0.0	0.0925	0.0925
2.800	.1488	.1488
3.235	.1729	.1729
11.73	.233	.221
36.86	.324	.302
74.01	.396	.344
116.2	.458	.366
184.2	.563	.394
213.7	.591	.406
255.9	.665	.430

In the last table the results show that the solutions contained not only the bicarbonate but the normal carbonate of calcium as well, and that with increasing quantities of sodium sulphate the quantity of calcium carbonate increased also.

Sodium chloride in the presence of gypsum as solid phase.

It will be observed by comparison of Tables LXXIII and LXXVII that the presence of calcium sulphate in solution depresses the solubility of calcium carbonate, as might be expected in the case of a salt in solution with a common ion. In both these tables the solubility of calcium carbonate passes through a maximum.

In the following table are given the results of experiments by Cameron and Seidell^a upon the solubility of gypsum and calcium carbonate in sodium chloride solutions, both gypsum and the carbonate being present as solid phases, and the solution being in equilibrium with the atmospheric air.

TABLE LXXVII.—*Solubility of calcium carbonate in aqueous solutions of sodium chloride, in contact with solid gypsum, in equilibrium with atmospheric air.*

CaSO ₄ per liter.	CaH ₂ (CO ₃) ₂ per liter.	NaCl per liter.
<i>Grams.</i>	<i>Gram.</i>	<i>Grams.</i>
1.9298	0.0603	0.0
2.720	.0724	3.628
3.446	.0885	11.49
5.156	.1006	39.82
6.424	.0603	79.52
5.272	.0563	121.9
4.786	.0482	193.8
4.462	.0402	267.6

Sodium chloride and sulphate.

An excess of solid calcium carbonate was added to solutions containing varying quantities of sodium chloride and sodium sulphate, and after three months at 25° C., with frequent shaking, the solutions were analyzed. Table LXXVIII gives the data obtained in this work.

TABLE LXXVIII.—*Solubility of calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C.*

Density 25° 25°	NaCl in—		Na ₂ SO ₄ in—		CaCO ₃ in 100 grams H ₂ O.
	100 c. c.	100 grams H ₂ O.	100 c. c.	100 grams H ₂ O.	
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>
1.2185	0.00	0.00	26.90	28.48	0.0239
1.2113	1.96	2.08	24.83	26.47	.0192
1.2115	6.43	6.93	21.67	23.36	.0137
1.2380	10.00	10.78	19.82	21.37	.0134
1.2378	10.07	10.89	19.39	20.98	.0137
1.2427	14.62	16.07	18.24	20.07	.0119
1.2570	17.16	19.18	18.43	20.74	.0116
1.2435	23.90	26.66	11.30	12.58	.0044
1.2442	27.30	31.15	8.79	10.00	.0046
1.2434	27.43	31.52	8.88	10.20	.0041
1.2270	28.32	32.17	6.74	7.65	.0043
1.2122	30.38	34.87	2.08	2.35	.0037
1.2020	31.52	35.70	0.00	0.00	.0036

^a Bul. No. 18, Division of Soils, U. S. Dept. Agr. (1901), p. 53.

These figures are in accord with the results of Cameron and Seidell, showing that calcium carbonate is more soluble in a saturated sodium sulphate solution than in one saturated with sodium chloride. It will be observed that as the concentration of sodium chloride in solution increases, the quantity of calcium carbonate decreases. The concentrations with respect to sodium chloride and sulphate are platted in figure 4. It has been found also that the presence of calcium carbonate in these small amounts has not appreciably affected the solubility of the more soluble chloride and sulphate of sodium.

In all these solutions calcium carbonate was the solid phase, and not a double compound. If a double compound of two calcium salts had been formed there would have been sodium carbonate in solution which would have caused the solutions to show a decided alkaline reaction. As the solutions were but very faintly, if at all, alkaline, no such change could have taken place. Further, if a double carbonate had resulted, the solution would have been rich in calcium salts and as the solution carried very little lime, it is apparent that such a change did not occur.

Owing to the very slight solubility of calcium carbonate in solutions of sodium chloride and sodium sulphate, it was expected that the presence of a salt (CaSO_4) with a common ion would depress this solubility even more. By the same procedure as was described in the preceding paragraph it was demonstrated that calcium carbonate underwent no change in these solutions.

TABLE LXXIX.—*Solubility of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C.*

Density 25° 25°	NaCl in—		Na ₂ SO ₄ in—		100g H ₂ O contains—	
	100 c. c.	100 grams H ₂ O.	100 c. c.	100 grams H ₂ O.	CaSO ₄	CaCO ₃
	Grams.	Grams.	Grams.	Grams.	Gram.	Gram.
1.2109	2.76	2.94	23.78	25.35	0.2290	0.0163
1.2113	5.52	5.93	21.97	23.39	.1992	.0155
1.2442	28.12	32.18	8.52	9.50	.0301	.0065

Sodium chloride and sodium sulphate with carbon dioxide.

The variance of the system—sodium sulphate, sodium chloride, calcium sulphate, calcium carbonate, and water saturated with carbon dioxide—is not increased over that of the preceding system by the addition of the new component carbon dioxide, if at the same time the further condition is imposed, that the pressure of the vapor phase equals atmospheric pressure. In this case a field will represent solutions in contact with two solid phases; a boundary line, solutions in contact with three solid phases. "Constant" solutions will be in equilibrium with four solid phases.

For the experimental work on this system solutions saturated with either sodium sulphate or sodium chloride were put in contact with an excess of calcium carbonate, and the several solutions were saturated with carbon dioxide by passing the gas under pressure into the solutions at a low temperature. The bottles were then shaken at constant temperature, 25° C., and frequently unstoppered so that the pressure of the vapor phase was finally the atmospheric pressure. In all cases solid calcium sulphate, either as gypsum or a double sulphate, was found. Table LXXX gives the analytical data obtained for this system:

TABLE LXXX.—*Solubility of mixtures of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate saturated with carbon dioxide at atmospheric pressure, at 25° C.*

Density 25° 25°	NaCl in—		Na ₂ SO ₄ in—		Calcium as calcium oxide in 100 grams H ₂ O.
	100 c. c.	100 grams H ₂ O.	100 c. c.	100 grams H ₂ O.	
	Grams.	Grams.	Grams.	Grams.	Gram.
1. 2158	0.00	0.00	25.86	27.12	0.1430
1. 2142	2.02	2.13	24.23	25.52	.1212
1. 2109	4.00	4.28	22.81	24.22	.1148
1. 2143	6.00	7.03	21.61	23.10	.1069
1. 2248	9.98	10.77	19.53	21.09	.0812
1. 2224	9.95	10.75	19.73	21.32	.0826
1. 2281	11.31	12.31	19.15	20.84	.0726
1. 2388	13.78	15.50	18.72	20.59	.0673
1. 2590	18.67	20.40	19.80	21.61
1. 2554	18.80	21.04	16.81	18.81	.0358
1. 2332	21.46	23.81	11.61	12.88
1. 2474	27.78	31.70	8.70	9.92	.0183
1. 2429	28.47	32.73	5.56	6.26	.0291
1. 2135	30.50	34.48	2.20	2.49	.0484
1. 1957	31.14	35.46	0.00	0.00	.0490

In figure 5 the points *A, B, C, D* represent the "constant" solutions in the simple case where sodium sulphate and sodium chloride only are in solution. Upon the addition of calcium carbonate and calcium sulphate the points are displaced somewhat, the new positions being represented by *A', B', C', D'*. This figure has been distorted somewhat to magnify some of the differences which if drawn to scale would not be recognizable. The quantity of lime salts in solution at these points is also widely different and this has been indicated by the width of the strip *A B C D D' C' B' A'*, the points *B* and *B'* and the

points *C* and *C'*, respectively, being close together. It has been found that over a certain range of concentrations, represented in the diagram by the field *B' C' F E*, gypsum is not the stable salt of calcium but a double sulphate of calcium and sodium, $3\text{Na}_2\text{SO}_4 \cdot 2\text{CaSO}_4$. Thus for every field there are two stable solid phases, one of which, calcium carbonate, exists over the whole figure. The other solid phases are sodium sulphate decahydrate, anhydrous sodium sulphate, sodium chloride, double sulphate, and gypsum for the fields marked 1, 2, 3, 4, and 5, respectively.

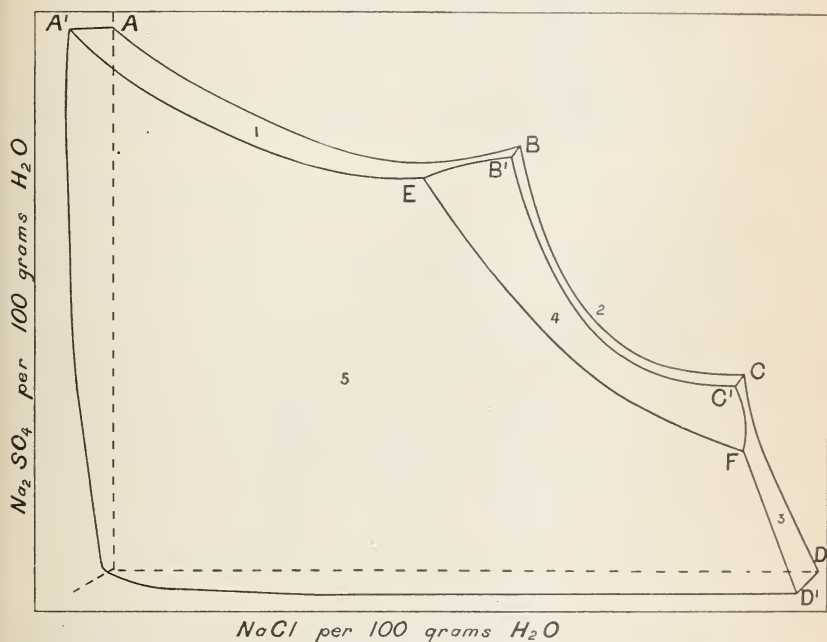


FIG. 5.—Diagram showing the solubility of calcium carbonate in solutions containing sodium chloride and sulphate, saturated with carbon dioxide at 25° C.

TABLE LXXXI.—Data for constant solutions in the system—sodium chloride, sodium sulphate, calcium sulphate, calcium carbonate, carbon dioxide, and water at 25° C.

Point.	Grams in 100 grams H ₂ O.			Solid phases.
	NaCl.	Na ₂ SO ₄ .	CaO.	
A	0.00	27.12	0.1430	Na ₂ SO ₄ .10H ₂ O, CaSO ₄ .2H ₂ O, and CaCO ₃ .
E	15.50	20.59	.0673	Na ₂ SO ₄ .10H ₂ O, CaSO ₄ .2H ₂ O, CaCO ₃ , and 2CaSO ₄ .3Na ₂ SO ₄ .
B	20.40	21.61	.0360	Na ₂ SO ₄ .10H ₂ O, CaCO ₃ , 2CaSO ₄ .3Na ₂ SO ₄ , and Na ₂ SO ₄ .
C	31.70	9.92	.0183	CaCO ₃ , NaCl, 2CaSO ₄ .3Na ₂ SO ₄ , and Na ₂ SO ₄ .
F	32.73	6.26	.0291	CaCO ₃ , NaCl, 2CaSO ₄ .3Na ₂ SO ₄ , and CaSO ₄ .2H ₂ O.
D	35.46	0.00	.0490	CaCO ₃ , NaCl, and CaSO ₄ .2H ₂ O.

Potassium chloride.

Cantoni and Goguelia^a have determined the solubility of calcium carbonate in solutions of potassium chloride as follows:

TABLE LXXXII.—*Solubility of calcium carbonate in potassium chloride.*

[Time of contact, 98 days at 12°–18° C.]

KCl in solution.	CaCO ₃ per liter.
<i>Per cent.</i>	<i>Gram.</i>
7.45	0.0748
10.0	.0742
20.0	.0828

It will be observed on comparison with Table LXX that potassium chloride has a greater solvent action on calcium carbonate than sodium chloride.

The following table contains results recently obtained in this laboratory:

TABLE LXXXIII.—*Solubility of calcium carbonate in aqueous solutions of potassium chloride at 25° C.*

Density $\frac{25^\circ}{25^\circ}$	KCl in solution.	CaCO ₃ in solution.
	<i>Per cent.</i>	<i>Per cent.</i>
1.000	0.00	0.0013
1.024	3.90	.0078
1.046	7.23	.0078
1.072	11.10	.0076
1.092	13.82	.0072
1.101	15.49	.0076
1.122	18.21	.0070
1.133	19.84	.0072
1.179	26.00	.0060

Potassium chloride and carbon dioxide.

The following table shows that the solubility of calcium carbonate in solutions of increasing content of potassium chloride passes through a maximum when the solutions are saturated with carbon dioxide:

TABLE LXXXIV.—*Solubility of calcium carbonate in aqueous solutions of potassium chloride saturated with carbon dioxide at atmospheric pressure at 25° C.*

KCl in solution.	CaCO ₃ in solution.
<i>Per cent.</i>	<i>Per cent.</i>
3.90	0.145
7.23	.150
11.10	.166
13.82	.165
15.49	.167
18.21	.154
19.84	.140
26.00	.126

^a Bul. Soc. Chim. (3), 33, 13 (1905).

Potassium sulphate.

The following table contains results obtained in this laboratory on the solubility of calcium carbonate in solutions of potassium sulphate at 25° C.:

TABLE LXXXV.—*Solubility of calcium carbonate in aqueous solutions of potassium sulphate at 25° C.*

Density $\frac{25^\circ}{25^\circ}$.	K ₂ SO ₄ in solution.	CaCO ₃ in solution.
	<i>Per cent.</i>	<i>Per cent.</i>
1.010	1.60	0.0104
1.021	3.15	.0116
1.033	4.73	.0132
1.048	6.06	.0148
1.061	7.85	.0168
1.069	8.88	.0192
1.083	10.18	.0192
1.084	10.48	.0188

Potassium sulphate and carbon dioxide.

When calcium carbonate dissolves in water carrying carbonic acid and potassium sulphate there is formed in the metathetical reaction calcium sulphate. There is enough potassium sulphate and calcium sulphate in solution to exceed the solubility of syngenite (K₂SO₄.CaSO₄.H₂O) and consequently above a certain concentration of potassium sulphate, syngenite is the stable solid and not calcium carbonate, all of which passes into solution. The following table gives the percentages of sulphuric acid and lime in solution for various points on the calcium carbonate and syngenite curves:

TABLE LXXXVI.—*Solubility of calcium carbonate in aqueous solutions of potassium sulphate saturated with carbon dioxide at atmospheric pressure at 25° C.*

SO ₃ in solution.	CaO in solution.
<i>Per cent.</i>	<i>Per cent.</i>
0.0	0.062
.69	.69
1.37	.69
1.67	.47
2.18	.30
2.99	.24

Sodium and potassium salts in general.

The precipitation of calcium carbonate in the cold is retarded or prevented by solutions of the alkali salts, chloride, sulphate, nitrate, carbonate, citrate, and phosphate,^a if the solutions are not too concentrated. According to Dulong the alkali sulphates, phosphates, phosphites, and arsenates decompose calcium carbonate on boiling.

^a Storer, Am. Jour. Sci. (2), **35**, 41 (1858); Dulong, Ann. Chim., **82**, 273 (1812); Spiller, Jour. Chem. Soc., **10**, 110 (1858); Kippenberger, Zeit. anorg. Chem., **6**, 177 (1894).

Sea water.

In a paper upon the action of sea water upon lime carbonate Irvine and Young^a have included results to show that the solubility of amorphous calcium carbonate in sea water was much greater than that of crystalline calcium carbonate. One part of amorphous calcium carbonate dissolves in 1,600 parts of sea water, while 8,000 parts of sea water are required to dissolve one part of crystalline calcium carbonate.

The following table contains the results of Anderson^b upon the relative solubilities of various forms of calcium carbonate in distilled water, in sea water, and in water saturated with carbon dioxide at 10° to 15° C.

TABLE LXXXVII.—*Solubility of carbonate of lime in distilled water, in sea water, and in solution saturated with CO₂.*

	Distilled water.		Sea water.		Water saturated with CO ₂ .	
	CaCO ₃ per liter.	Time.	CaCO ₃ per liter.	Time.	CaCO ₃ per liter.	Time.
	<i>Gram.</i>	<i>Hours.</i>	<i>Gram.</i>	<i>Hours.</i>	<i>Gram.</i>	<i>Hours.</i>
Calc-spar, massive.....	0.0147	120	0.0075	47		
Do.....			.0046	120		
Do.....			.0000	396	0.0815	24
Granular.....					.1285	24
Fine ground.....					.2036	24
Impalpable powder.....	.0251	46	.0082	47	.4720	24
Do.....			.0052	120		
Do.....			.0000	396		
Coral.....	.0285	96	.0237	96		
Amorphous CaCO ₃2480		.6100			

The table shows that upon long standing in contact with the solvent the calcium carbonate in solution decreases, indicating the formation of a less soluble modification of calcium carbonate. It is also shown that the rate at which the solid is dissolved is increased by grinding the solid to a powder.

The solubility of calcium carbonate in an artificial sea water has been determined by Cohen and Raken^c by agitating the mixture with a current of air. After 8 days at 15° C., 53.94 milligrams CaCO₃ were found in one liter, and after 17 days 57.27 milligrams CaCO₃ per liter.

Ammonium salts.

The presence of ammonium salts tends to hold calcium carbonate in solution, even in the case of the carbonate of ammonium which might be expected to cause complete precipitation of calcium carbonate. The solubility of calcium carbonate has been shown to be

^a Proc. Roy. Soc. Edinburgh, **15**, 316 (1888).

^b Proc. Roy. Soc. Edinburgh, **16**, 319 (1889).

^c Proc. K. Akad. Wetensch. Amsterdam, **3**, 63 (1900); abstr. in Jour. Chem. Soc., **72** ii, 725 (1900).

increased in the presence of the chloride, carbonate, sulphate, nitrate, acetate, and succinate of ammonium.^a Bertrand has given the amounts of different ammonium salts which are required to hold in solution 1 gram of calcium carbonate, viz, 13.98 grams ammonium chloride, 8.38 grams ammonium sulphate, and 14.44 grams ammonium nitrate, but the absolute concentrations are not given. When the solution of calcium carbonate in ammonium chloride is heated to boiling there is decomposition with the formation of ammonia and carbon dioxide.^b The same decomposition has been shown in the case of the other ammonium salts, sulphate, sulphite, phosphate, phosphite, and oxalate.^c On cooling the solutions of calcium carbonate in ammonium salts, the solid carbonate crystallizes out.

Calcium and magnesium salts.

Calcium carbonate is soluble in dilute solutions of calcium and magnesium sulphates and chlorides.^d According to Hunt a solution containing 3 or 4 grams of magnesium sulphate per liter will dissolve over 1 gram of calcium carbonate. It is also soluble in calcium succrate.^e

When calcium acetate solution is added to potassium carbonate solution, the precipitate is not calcium carbonate, but a double carbonate of calcium and potassium, $\text{CaK}_2(\text{CO}_3)_2$.^f

The action of water carrying carbon dioxide and the chloride of lime or magnesia upon various lime algæ has been investigated by Vesterberg.^g In the presence of sodium chloride relatively more magnesia is dissolved than in the presence of calcium chloride or in the presence of magnesium chloride.

Other compounds.

Compounds which give acid solutions, such as stannic chloride and the chloride or nitrate of iron, aluminum or chromium, dissolve calcium carbonate with the evolution of carbon dioxide. As the acidity is reduced the hydroxide or oxide is precipitated. Calcium carbonate is not acted upon by concentrated nitric acid,^h for it becomes coated with calcium nitrate, which is insoluble in the concentrated acid. Upon the addition of water, however, a brisk action begins.

^a Wittstein, *Repert. Pharm.* (2), **7**, 18 (1836); Smith, *Phil. Mag.* (3), **9**, 542 (1836); Brett, *Phil. Mag.* (3), **10**, 95 (1837); Wackenroder, *Ann. Chem. Pharm.*, **41**, 315 (1842); Fresenius, *Ann. Chem. Pharm.*, **59**, 117 (1846); Storer, *Am. Jour. Sci.* (2), **25**, 41 (1858); Bertrand, *Monit. Sci.* (3), **10**, 477 (1880).

^b Demarçay, *Ann. Chim.* (2), **55**, 398 (1834); Schriebe, *Zeit. angew. Chem.*, **2**, 211 (1889); Cantoni and Goguelia, *Bul. Soc. Chim.* (3), **31**, 282 (1904); **33**, 13 (1905).

^c Dulong, *Ann. Chim.*, **82**, 273 (1812).

^d Cousté, *Compt. rend.*, **35**, 186 (1852); Hunt, *Am. Jour. Sci.* (2), **26**, 109 (1858).

^e Barreswill, *Jour. Pharm.* (3), **19**, 330 (1851).

^f Reynolds, *Jour. Chem. Soc.*, **73**, 262 (1898).

^g *Bul. Geol. Inst. Upsala*, **5**, 97 (1900); **6**, 254 (1903).

^h Barreswill, *Jour. Pharm.* (3), **3**, 290 (1843).

The rate at which calcium carbonate in the form of Iceland spar is dissolved by acids has been shown by Spring ^a to be independent of the chemical nature of inorganic acids whose calcium salts are soluble. It was also proved that the velocity depended upon the surface exposed, and that at low temperatures the rate was proportional to the concentration of the acid.

In solutions of hydrochloric and nitric acids in absolute ethyl alcohol, calcium carbonate is readily attacked, but not by solutions of sulphuric acid.^b The same results have been found for solutions of these acids in the other organic solvents, acetone and methyl alcohol.^c The addition of water to the sulphuric acid mixture causes the reaction to be very much accelerated. Acetic acid acts similarly to sulphuric acid. In all these cases the occurrence of chemical reaction depends on the solubility or insolubility of the calcium salt of the acid in the solvent employed.

GENERAL CONCLUSIONS.

1. Calcite is the stable form of calcium carbonate at ordinary temperatures. In concentrated salt solutions or at the higher concentrations, aragonite is probably the stable phase.

2. Regarding the formation of natural dolomite, the literature affords no satisfactory explanation. High temperatures and concentrated solution seem to be necessary for its formation.

3. At the low temperatures calcium carbonate forms a hydrate with five molecules of water of crystallization.

4. The results upon the solubility of calcium carbonate in water are very discordant, but there is good authority for the generalization that it is more soluble in hot water than in cold.

5. The solubility of calcium carbonate in water containing carbon dioxide increases as the quantity of carbon dioxide in solution increases.

6. The solubility of calcium carbonate is depressed by the addition of caustic soda to the solution.

7. The caustification of sodium carbonate by lime is more complete in dilute solution.

8. Calcium carbonate forms with sodium carbonate two double compounds, whose stability depends on the temperature and the concentration of the solution with which they are in contact.

9. The solubility of calcium carbonate is increased by addition of sodium chloride or of sodium sulphate.

^a Bul. Acad. Roy. Belg. (3), **14**, 725 (1887); Bul. Soc. Chim. (3), **3**, 177 (1890).

^b Carette, Thesis, Lille, 1900. See Vallée, Compt. rend., **132**, 677 (1901).

^c Vallée, Loc. cit.

10. When the pressure of carbon dioxide is one atmosphere, the solubility of calcium carbonate passes through a maximum upon increasing the concentration of sodium chloride in solution, both in the presence and absence of gypsum. When increasing quantities of sodium sulphate are added, however, the solubility of the carbonate constantly increases.

11. The solubility of calcium carbonate at 25° C. is about six times as great in a saturated solution of sodium sulphate as in a saturated solution of sodium chloride.

12. When certain solutions containing sodium sulphate and chloride are saturated with carbon dioxide in the presence of calcium carbonate a new solid phase appears, $2\text{CaSO}_4 \cdot 3\text{Na}_2\text{SO}_4$.

13. When the pressure of carbon dioxide is one atmosphere, the solubility of calcium carbonate passes through a maximum upon increasing the concentration of potassium chloride or sulphate in solution.

14. In the presence of sea water the crystalline modification of calcium carbonate is more stable than the amorphous form.

15. In general the presence of ammonium salts in solution increases the solubility of calcium carbonate. On heating, carbon dioxide and ammonia escape.

16. Calcium and magnesium salts have a solvent action upon calcium carbonate.

17. Salt solutions which have an acid reaction tend to dissolve calcium carbonate.

18. Calcium carbonate is soluble in strong acids, whose lime salts are soluble in the strong acid.

MAGNESIA.

SOLUBILITY OF MAGNESIA IN WATER.

The wide variations between the results of the various observers have been attributed by Whipple and Mayer to two causes—the solvent action of carbon dioxide dissolved from the air and the action of water upon the glass vessels in which the solutions were contained. Water reacts with many kinds of glass, dissolving the bases; and as some of the determinations were made by estimating the alkalinity of the solution, this quantity of alkali dissolved from the glass walls introduced very large errors. To these two causes of discrepancy might be added a third probable source of error. The presence of very minute quantities of impurities in the magnesia, such as lime, would introduce comparatively large errors into the determinations of the solubility of magnesia. The following table gives the results of the various observers.

TABLE LXXXVIII.—*Solubility of magnesium hydroxide in water.*

Mg(OH) ₂ per liter.	Temperature.	Observer.
<i>Milligrams.</i>	<i>°C.</i>	
250	15	Fyfe. ^a
250	15	Henry. ^b
26	(Hot and cold.)	Fresenius. ^c
5-10	(Cold.)	Bineau. ^d
9	18	Kohlrausch and Rose. ^e
8	18	Dupré and Bialas. ^f
12	22	Whipple and Mayer. ^g

^a Cited by Henry, Jour. Pharm., 13, 1 (1827).^b Jour. Pharm., 13, 1 (1827).^c Ann. Chem. Pharm., 59, 117 (1847).^d Compt. rend., 41, 510 (1855).^e Zeit. phys. Chem., 12, 241 (1893).^f Zeit. angew. Chem., 16, 54 (1903).^g Jour. Infectious Diseases, Suppl. No. 2, 151 (1906).

SOLUBILITY OF MAGNESIA IN AQUEOUS SOLUTIONS.

The solubility of magnesia is given by Precht ^a as 16 milligrams per liter in water containing potash. The presence of ammonium salts increases the solubility of magnesia, even in the presence of free ammonia.^b When warm solutions of ammonium salts are decomposed by magnesia, ammonia is evolved. Sodium and potassium salts act similarly in their solvent action on magnesia but to a far lesser degree.^c Maigret ^d has recently investigated the solubility of magnesia in a sodium chloride solution containing sodium hydroxide and shows that the presence of the free base reduces the solubility.

TABLE LXXXIX.—*Solubility of magnesia in solutions of sodium chloride containing sodium hydroxide.*

NaCl per liter.	MgO per liter.	
	With 0.8 gram NaOH per liter.	With 4.0 grams NaOH per liter.
<i>Grams.</i>	<i>Gram.</i>	<i>Gram.</i>
125	0.07	0.03
140	.045	.0
160	.0	.0

The solubility of magnesia is increased by glucose.^e Bernard and Ehrmann^f have, however, used the insolubility of magnesia in sugar solutions as a means of separating lime and magnesia. The following

^a Zeit. anal. Chem., 18, 439 (1879).^b Warrington, Jour. Chem. Soc., 18, 27 (1865); Lovén, Zeit. anorg. Chem., 11, 404 (1896); Treadwell, Zeit. anorg. Chem., 37, 326 (1903); Herz and Muhs, Zeit. anorg. Chem., 38, 138 (1904).^c Warrington, Jour. Chem. Soc., 18, 27 (1865).^d Bul. Soc. Chim. (3), 33, 631 (1905).^e Fleury, Jour. Pharm. (4), 28, 400 (1878).^f Compt. rend., 83, 1239 (1876).

table of Herz and Muhs ^a gives the solubility of magnesium hydroxide in solutions containing ammonium salts:

TABLE XC.—*Solubility of magnesia in ammonium salt solutions at 29° C.*

NH ₄ Cl per liter.	Mg(OH) ₂ per liter.	NH ₄ NO ₃ per liter.	Mg(OH) ₂ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
4.13	1.43	6.09	1.45
5.67	1.86	14.69	2.43
9.21	2.60
13.39	3.15
20.86	4.55

When recently ignited magnesia is added to a concentrated solution of magnesium chloride a very thick mass is formed which according to Sorel ^b is composed of an oxychloride of magnesium. Bender ^c has given it the formula $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 17\text{H}_2\text{O}$, Davis ^d the formula $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 13\text{H}_2\text{O}$, and Krause ^e the formula $\text{MgCl}_2 \cdot 10\text{MgO} \cdot 14\text{H}_2\text{O}$ when dried at 110°, and $\text{MgCl}_2 \cdot 10\text{MgO} \cdot 18\text{H}_2\text{O}$ when air dried. André ^f has found the heat of formation of the following oxychlorides, $\text{MgCl}_2 \cdot \text{MgO} \cdot 16\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot \text{MgO} \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 10\text{MgO} \cdot 13\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 10\text{MgO} \cdot 16\text{H}_2\text{O}$. The following crystalline basic bromides of magnesium have been prepared by Tassilly, ^g $\text{MgBr}_2 \cdot 3\text{MgO} \cdot 12\text{H}_2\text{O}$, $\text{MgBr}_2 \cdot 3\text{MgO} \cdot 6\text{H}_2\text{O}$.

GENERAL CONCLUSIONS.

1. The various determinations of the solubility of magnesia in water are not in accord. The modern writers, however, agree that this solubility is about 10 milligrams per liter at 20° C.
2. The solubility of magnesia is augmented by various salts, including magnesium salts, but is depressed by caustic alkalies.
3. Several basic chlorides and bromides of magnesium have been recorded in the literature, and are obtained by adding magnesia to a solution of the chloride or bromide of magnesium.

MAGNESIUM CARBONATE.

MODIFICATIONS AND HYDRATES OF MAGNESIUM CARBONATE.

The mineral magnesite is probably insoluble in water ^h and is not affected by boiling with water or aqueous solutions of alkaline carbonates. Artificial magnesium carbonate has been prepared by Engel ⁱ

^a Zeit. anorg. Chem., **38**, 140 (1904).

^b Compt. rend., **65**, 102 (1867).

^c Ann. Chem. Pharm., **159**, 341 (1871).

^d Chem. News, **25**, 258 (1872).

^e Ann. Chem. Pharm., **165**, 38 (1873).

^f Compt. rend., **94**, 444 (1882).

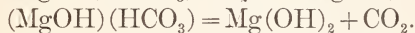
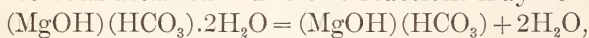
^g Compt. rend., **125**, 605 (1897); Bul. Soc. Chim. (3), **17**, 964 (1897).

^h See Davis, Jour. Soc. Chem. Ind., **25**, 788 (1906).

ⁱ Compt. rend., **129**, 598 (1899).

by heating to 130° C. the double carbonate of magnesium and ammonium. This anhydrous magnesium carbonate "slakes" in moist air, being easily converted into the hydrated form $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. On account of its behavior when heated Davis has given it the formula $(\text{MgOH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$, 2 molecules of water being lost when the compound is heated to 95° or 100° C., at which temperature the substance becomes constant in weight as soon as the composition $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ or $(\text{MgOH})(\text{HCO}_3)$ is reached. At 125° C. the rate of change is very much more rapid. This same change can be brought about by heating the compound $(\text{MgOH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$ with xylene, the water which is liberated being removed as fast as it is formed and consequently hydrolysis of the salt can not ensue.

By heating the above compound with water, however, a product is obtained of widely varying composition, depending upon the time and upon the temperature. The product has been considered as a basic carbonate of magnesium. Davis, however, by a microscopical examination has proved that it is in all cases a mixture of two solid phases and not a single compound. As the dehydration of the compound $(\text{MgOH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$ requires considerable time and as the equilibrium between the compound $(\text{MgOH})(\text{HCO}_3)$ and the hydroxide of magnesium is reached but slowly, the solid residue was found to consist of two and often three solid phases, indicating that equilibrium had not been attained. The two reactions may be written:



The solid phases consisted of the two hydrates of magnesium carbonate and of magnesium hydroxide.

When a magnesium salt is precipitated by means of a solution of an alkaline carbonate, a basic carbonate, or a double carbonate may first be formed, but experiments by Berzelius,^a Fritzsche,^b Favre,^c Jacquelin,^d and Rose^e have proved that upon standing for several days the precipitate becomes crystalline and corresponds to the formula $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. Kippenberger^f has ascribed the formula $\text{MgCO}_3 \cdot \frac{1}{4}\text{H}_2\text{O}$ to this compound and Marignac^g and Damour^h have obtained $\text{MgCO}_3 \cdot 4\text{H}_2\text{O}$.

^a Ann. Chim. Phys. (2), **14**, 363 (1820).

^b Ann. Phys. Chem., **37**, 304 (1836).

^c Ann. Chim. Phys. (3), **10**, 474 (1844).

^d Ann. Chim. Phys. (3), **32**, 195 (1851).

^e Ann. Phys. Chem., **84**, 461 (1851).

^f Zeit. anorg. Chem., **6**, 177 (1894).

^g Compt. rend., **42**, 288 (1856).

^h Compt. rend., **44**, 561 (1857).

DOUBLE CARBONATES CONTAINING MAGNESIUM CARBONATE.

When carbon dioxide is passed into a suspension of magnesia to saturation the solution contains 10.7 grams of magnesia (MgO) in one liter and when an equal volume of 95 per cent alcohol is added a precipitate of magnesium carbonate forms, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.^a

By mixing solutions of a soluble magnesium salt with a solution of an alkaline carbonate various compounds have been obtained:^b $\text{K}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$, $\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$, and $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 15\text{H}_2\text{O}$. Kippenberger^c has shown that the precipitate obtained by mixing sodium carbonate and magnesium sulphate in equimolecular proportions is soluble in the alkaline bicarbonates. After several hours, however, the hydrated magnesium carbonate separates in large crystals and the quantity of magnesium carbonate in solution decreases after several days. Freshly precipitated magnesium carbonate is soluble in magnesium chloride and in magnesium sulphate solutions.

The double carbonates of sodium and magnesium undergo decomposition upon heating in water, sodium carbonate passing into solution and the solid residue consisting of a mixture of magnesium hydroxide and carbonate.^d It is difficult, however, to remove the last traces of the alkali from the solid, even by boiling, and in order to obtain pure magnesium carbonate Davis has dissolved the solid residue in water saturated with carbon dioxide and then boiled off the carbon dioxide, leaving a residue free from traces of sodium salts.

SOLUBILITY OF MAGNESIUM CARBONATE IN AQUEOUS SOLUTIONS.

Carbon dioxide.

Owing to the slow transformation of one modification into another, the solubility of magnesium carbonate in water and in aqueous solutions depends upon the source of the solid employed and on the time of contact. Engel^e has given the results of Beckurts and of Bineau, who undoubtedly worked with widely different samples and under different conditions. One liter of water saturated with carbon dioxide dissolves 1.31 grams magnesium carbonate according to Wagner and Merckel, 8.39 grams according to Beckurts, and 23.3 grams according to Bineau. The following table gives the results of Wagner and Merckel,^f who found the effect of increasing the quantity of carbon dioxide in solution:

^a Monhaupt, Chem. Zeit., **28**, 868 (1904).

^b See Graham-Otto, Lehrbuch anorg. Chem., 5th edn., III, 730-753.

^c Zeit. anorg. Chem., **6**, 177 (1894).

^d Davis, loc. cit.

^e Ann. Chim. Phys. (6), **13**, 344 (1888).

^f Jour. prakt. Chem., **102**, 233 (1867).

TABLE XCI.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at 5° C.*

Pressure.	MgCO ₃ per liter.
<i>Atmospheres.</i>	<i>Grams.</i>
1	1.31
2	1.34
3	7.46
4	9.03
5	9.09
6	13.15

Engel and Ville ^a have also found that by increasing the pressure of the carbon dioxide and by decreasing the temperature the quantity of magnesium carbonate in solution increased.

TABLE XCII.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various pressures (Engel and Ville).*

T=19.5° C.		T=12° C.	
Pressure.	MgCO ₃ per liter.	Pressure.	MgCO ₃ per liter.
<i>Atmospheres.</i>	<i>Grams.</i>	<i>Atmospheres.</i>	<i>Grams.</i>
1	25.79	0.5	20.5
2.1	33.11	1	26.5
3.2	37.30	1.5	31.0
4.7	43.50	2	34.0
5.6	46.20	2.5	36.4
6.2	48.50	3	39.0
7.5	51.20	4	42.8
9.0	56.59	6	50.6

TABLE XCIII.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various temperatures. Pressure = 1 atmosphere (Engel and Ville).*

Temperature.	MgCO ₃ per liter.
<i>° C.</i>	<i>Grams.</i>
13.4	28.45
19.5	25.79
29.3	21.95
46.0	15.7
62.0	10.35
70.0	8.1
82.0	4.9
90.0	2.4
100.0	0.0

TABLE XCIV.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various temperatures. Pressure = 1 atmosphere (Engel).*

Temperature.	MgCO ₃ per liter.
<i>° C.</i>	<i>Grams.</i>
3.5	36.5
12.0	26.5
18.0	22.1
22.0	20.0
30.0	15.8
40.0	11.8
50.0	9.5

^a Compt. rend., 93, 340 (1881); see also Engel, Compt. rend., 100, 444 (1885); Ann. Chim. Phys. (6), 13, 344 (1888).

Bodländer ^a has attempted to obtain a formula of the same form as that derived to express the solubility of calcium carbonate in water containing carbon dioxide, but has found it necessary to assume the presence of ions in solution of the form $(\text{MgCO}_3)_n\text{MgOH}$.

Finally, Treadwell and Reuter ^b have shown that at the lower concentrations there is less carbon dioxide in solution than corresponds to the formula $\text{MgH}_2(\text{CO}_3)_2$, a conclusion which has been confirmed by Rinne. ^c These results are shown in the following table:

TABLE XCV.—*Solubility of magnesium carbonate in water containing carbon dioxide at 12° to 15° C. (average, 14° C.).*

Partial pressure of CO_2 .	CO_2 per 100 c.c. solution.	$\text{MgH}_2(\text{CO}_3)_2$ per 100 c.c. solution.	MgCO_3 per 100 c.c. solution.
<i>Millimeters.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>
143.3	119.0	1,210.5
41.6	86.6	1,210.5
33.8	3.5	1,210.5
11.7	1,076.6	77.3
10.3	762.9	76.5
8.2	595.2	80.7
4.7	366.3	70.1
4.6	341.7	75.8
2.5	263.2	74.8
1.6	222.9	77.1
1.1	216.9	71.0
0.3	203.6	71.1
.....	203.3	68.5
.....	196.0	70.2
.....	203.6	62.5
.....	195.4	61.6
.....	195.4	64.1

Rinne ^d has boiled a solution of magnesium carbonate in water containing carbon dioxide for several hours, and found that the quantity of magnesia in solution constantly decreased.

Sodium chloride.

The solubility of magnesium carbonate in various aqueous solutions of sodium salts has been recorded by Cameron and Seidell. ^e

TABLE XCVI.—*Solubility of magnesium carbonate in solutions of sodium chloride free of carbon dioxide.*

Weight of liter solution.	NaCl per liter.	MgCO_3 per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>
996.92	0.0	0.176
1,016.82	28.0	.418
1,041.09	59.5	.527
1,070.50	106.3	.585
1,094.53	147.4	.544
1,142.48	231.1	.460
1,170.14	272.9	.393
1,199.28	331.4	.293

^a Zeit. phys. Chem., 35, 23 (1900).

^b Zeit. anorg. Chem., 17, 170 (1898).

^c Chem. Zeit., 31, 125 (1907).

^d Loc. cit.

^e Jour. Phys. Chem., 7, 578 (1903).

Sodium chloride and carbon dioxide.

TABLE XCVII.—*Solubility of magnesium carbonate in solutions of sodium chloride saturated with atmospheric air at 25° C.*

NaCl per liter.	Mg(HCO ₃) per liter.
<i>Grams.</i>	<i>Grams.</i>
7.0	30.64
56.5	30.18
119.7	27.88
163.9	24.96
224.8	20.78
306.6	10.75

Sodium sulphate.

TABLE XCVIII.—*Solubility of magnesium carbonate in solutions of sodium sulphate free of carbon dioxide.*

24° C.			35° C.		
Weight of liter solution.	Na ₂ SO ₄ per liter.	MgCO ₃ per liter.	Weight per liter solution.	Na ₂ SO ₄ per liter.	MgCO ₃ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
997.52	0.0	0.216	995.15	0.32	0.131
1,021.24	25.12	.586	1,032.89	41.84	.577
1,047.60	54.76	.828	1,067.23	81.84	.753
1,080.95	95.68	1.020	1,094.77	116.56	.904
1,133.85	160.80	1.230	1,120.38	148.56	.962
1,157.34	191.90	1.280	1,151.70	186.7	1.047
1,206.03	254.60	1.338	1,179.82	224.0	1.088
1,223.91	278.50	1.338	1,196.32	247.2	1.110
1,241.99	305.10	1.388	1,236.52	299.2	1.130

GENERAL CONCLUSIONS.

1. Magnesium carbonate forms several hydrates, each of which is stable within limits of concentration and temperature.
2. Magnesium carbonate forms several double compounds with the alkali carbonates.
3. The solubility of magnesium carbonate is greatly increased by the addition of carbon dioxide to the solution, the solubility being less at the higher temperatures.
4. The solubility of magnesium carbonate passes through a maximum as the concentration of sodium chloride increases, but in the presence of carbon dioxide this solubility is depressed by addition of sodium chloride.
5. The solubility in solutions of sodium sulphate is increased by increasing the concentration of the latter.

